

## Kinetics and mechanism of polymerization initiated by manganic ion-ethoxyacetic acid redox system—A study on the reactivity of vinyl monomers

T BALAKRISHNAN\*<sup>1</sup>, S SUBBU<sup>2</sup> and K RAVISANKAR<sup>2</sup>

<sup>1</sup>Department of Physical Chemistry, University of Madras, Madras 600 025, India

<sup>2</sup>Department of Chemistry, Pachaiyappa's College, Madras 600 030, India

MS received 19 April 1988

**Abstract.** The kinetics of polymerization of acrylic acid (AA) and methacrylamide (MAM) initiated by the redox system  $Mn^{3+}$ -ethoxyacetic acid (EAA) in aqueous sulphuric acid was studied at 35°C. The polymerization of both the monomers followed the same mechanism, viz., initiation by the primary radical arising from the oxidation of EAA and termination by the  $Mn^{3+}$  ion. The rate coefficients  $k_i/k_0$  and  $k_p/k_t$  were correlated to monomer and polymer radical reactivities, respectively. Acrylic acid was found to have higher monomer and polymer radical reactivities than methacrylamide.

**Keywords.** Polymerization; acrylic acid; methacrylamide; reactivity.

### 1. Introduction

Several organic substrates (Gangadevi and Mahadevan 1972, 1973; Elayaperumal *et al* 1979, 1980; Balakrishnan and Subbu 1986) coupled with  $Mn^{3+}$  ion have been used as efficient redox systems for the initiation of vinyl polymerization. A survey of the literature showed that  $Mn^{3+}$ -substrate redox systems were used as initiators in the study of the reactivities of vinyl monomers only in a few cases (Elayaperumal *et al* 1982; Balakrishnan and Subbu 1988). In this paper we report the results of our kinetic investigation of polymerization of acrylic acid and methacrylamide initiated by the  $Mn^{3+}$ -ethoxyacetic acid redox system. This paper also attempts to compare the reactivities of the two monomers and polymer radical reactivities in homopolymerization.

### 2. Experimental

Manganese(III) acetate dihydrate was prepared by adopting the literature procedure (Andrulis *et al* 1966). Acrylic acid used was distilled twice over cupric chloride under reduced pressure (b.p. 50°C at 15 mm Hg). Methacrylamide was recrystallized from an alcohol-benzene mixture. Ethoxyacetic acid was prepared as per

\*For correspondence

Fuson and Wojcik (1933). Sulphuric acid, sodium bisulphate and all other chemicals used were of analar grade.

Polymerization was carried out in reaction tubes in a nitrogen atmosphere. The rate of polymerization was followed by bromometry and the rate of  $Mn^{+3}$  ion disappearance was followed by iodometry. All the experiments were carried out in aqueous sulphuric acid media.

### 3. Results and discussion

Polymerization of acrylic acid and methacrylamide initiated by  $Mn^{3+}$ -ethoxyacetic acid redox system takes place at measurable rates at 35°C. An induction period was observed in aerated conditions whereas it was not noticed in deaerated conditions.

In our study the polymerization kinetics of acrylic acid is analogous to that of methacrylamide in several respects. Hence the two systems are discussed together. Steady state rate of polymerization was reached in 5 minutes in both the systems.

#### 3.1 The rate of polymerization, $R_p$

The rate of polymerization is found to be dependent on the first power of monomer concentration in the polymerization of both the monomers. The plots of  $\log R_p$  vs.  $\log [M]$  are linear with a slope of unity (figures 1A and 2A). The plots of  $R_p$  vs.  $[M]$  give straight lines with zero intercepts thereby indicating that the order with respect to  $[M]$  is unity (figures 1B and 2B).

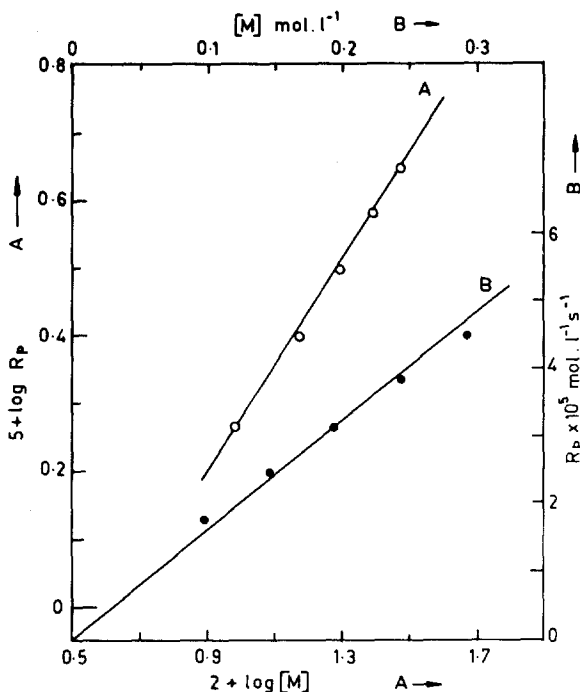


Figure 1. (A) Plot of  $\log R_p$  vs.  $\log [M]$ . (B) Plot of  $R_p$  vs.  $[M]$  at constant  $[EAA] = 5 \times 10^{-3}$  M,  $[Mn^{3+}] = 2.37 \times 10^{-3}$  M,  $[H^+] = 2.0$  M,  $\mu = 2.4$  M, and  $T = 35^\circ\text{C}$ .

The dependence of  $R_p$  on [EAA] is investigated by varying the concentration of EAA at constant [M],  $[Mn^{3+}]$ ,  $[H^+]$ ,  $\mu$  and temperature. The plots of  $\log R_p$  vs.  $\log [EAA]$  are linear with a slope of unity (figures 3A and 4A). The plots of  $R_p$  vs. [EAA] are straight lines passing through the origin (figures 3B and 4B). These plots show that the order with respect to [EAA] is unity.

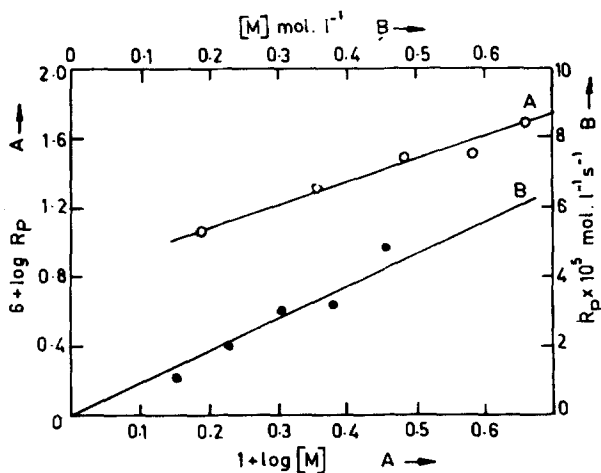


Figure 2. (A) Plot of  $\log R_p$  vs.  $\log [M]$  (B) Plot of  $R_p$  vs.  $[M]$  at constant EAA =  $5 \times 10^{-3}$  M,  $[Mn^{3+}] = 1.74 \times 10^{-3}$  M,  $[H^+] = 2.0$  M,  $\mu = 2.4$  M and  $T = 35^\circ\text{C}$ .

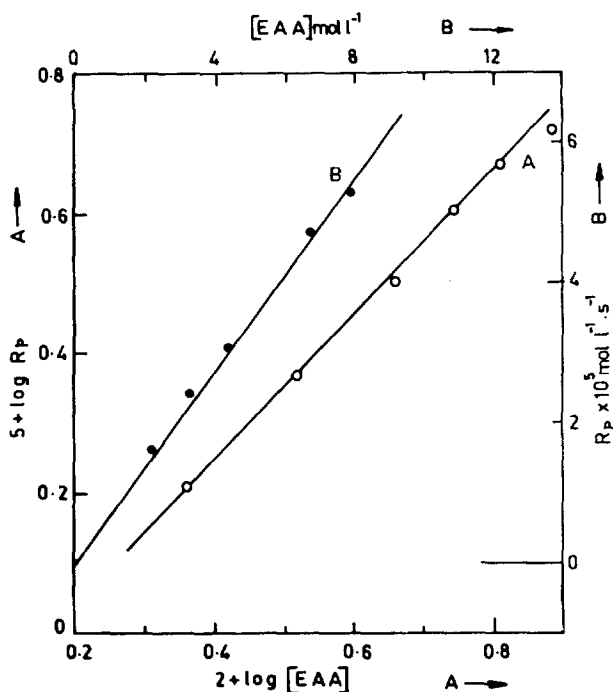
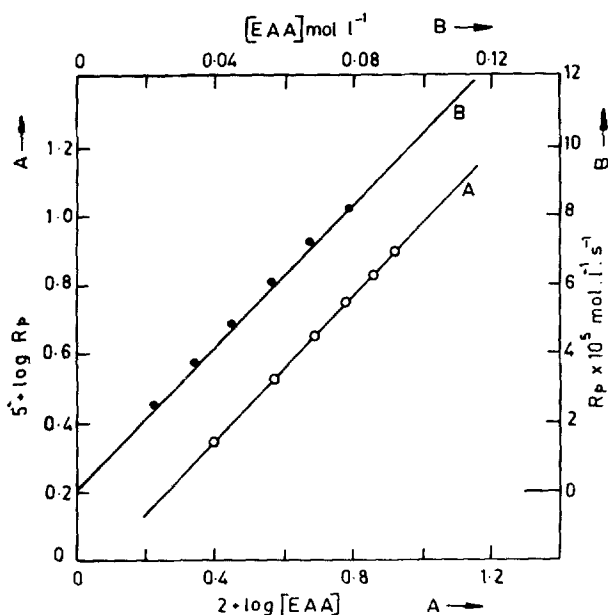


Figure 3. (A) Plot of  $\log R_p$  vs.  $\log [EAA]$ . (B) Plot of  $R_p$  vs.  $[EAA]$  at constant monomer = 0.09758 M,  $[Mn^{3+}] = 2.31 \times 10^{-3}$  M,  $[H^+] = 2.0$  M,  $\mu = 2.4$  M and  $T = 35^\circ\text{C}$ .



**Figure 4.** (A) Plot of  $\log R_p$  vs.  $\log [EAA]$ . (B) Plot of  $R_p$  vs.  $[EAA]$  at constant monomer = 0.1055 M,  $[Mn^{3+}] = 2.18 \times 10^{-3}$  M,  $[H^+] = 2.0$  M,  $\mu = 2.4$  M and  $T = 35^\circ\text{C}$ .

$R_p$  is observed to be almost independent of  $Mn^{3+}$  ion concentration in both the systems. This observation indicates that the termination of polymerization may be effected by  $Mn^{3+}$ .

In both the systems, there is no significant change in  $R_p$  as the  $[H^+]$  is increased at constant ionic strength. Similarly variation of ionic strength at constant  $[H^+]$  has only very little effect on  $R_p$ .

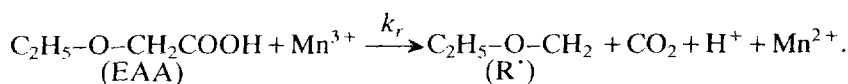
### 3.2 Rate of manganic ion disappearance ( $-R_m$ )

The following observations are common for both the monomers.  $-R_m$  has a first order dependence on  $[Mn^{3+}]$ . The plots of  $-R_m$  vs.  $[Mn^{3+}]$  are straight lines with zero intercepts (figures 5A and 5B).  $-R_m$  increases linearly with increase in the concentration of EAA.  $-R_m$  is not affected by the increase in monomer concentration, showing that the polymerization is not initiated by  $Mn^{3+}$  ion under the experimental conditions.  $-R_m$  is also not affected significantly by the change in  $[H^+]$  and ionic strength.

### 3.3 Reaction mechanism and rate law

The kinetic features mentioned above can be adequately explained on the basis of the following reaction scheme.

*Formation of free radical*



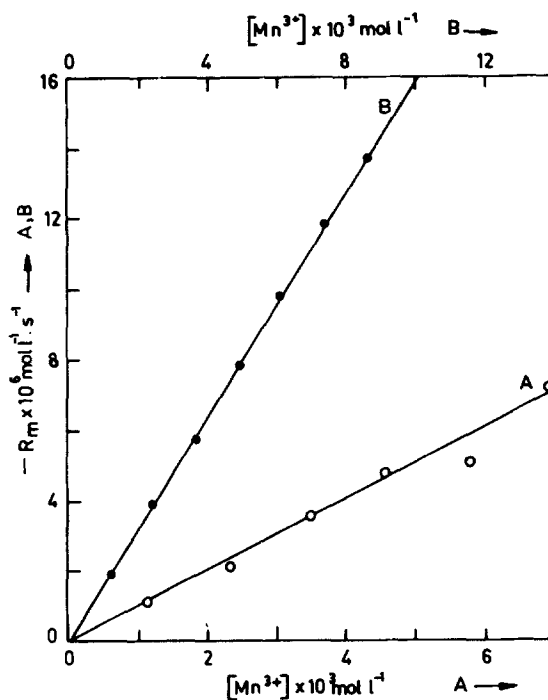
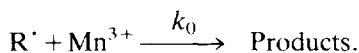
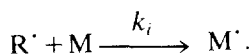


Figure 5. (A) Plot of  $-R_m$  vs.  $[Mn^{3+}]$  (for the acrylic acid system) at constant monomer = 0.09756 M,  $[EAA] = 0.075$  M,  $[H^+] = 2.0$  M,  $\mu = 2.4$  M and  $T = 35^\circ C$ . (B) Plot of  $-R_m$  vs.  $[Mn^{3+}]$  (for methacrylamide system) at constant monomer = 0.1055 M,  $[EAA] = 0.075$  M,  $[H^+] = 2.0$  M,  $\mu = 2.4$  M and  $T = 35^\circ C$ .

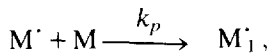
Reaction of primary radical with  $Mn^{3+}$



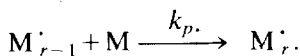
Initiation



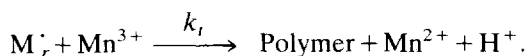
Propagation



.....  
 .....



Termination



By adopting the stationary state assumption for the free radical concentrations and the principle of non-dependence of rate constants ( $k_p$  and  $k_t$ ) on the chain lengths, the following expressions for  $R_p$  and  $-R_m$  are obtained

$$R_p = \frac{k_p k_r [\text{EAA}] [\text{M}]^2}{k_t([\text{M}] + (k_0/k_i) [\text{Mn}^{3+}])}, \quad (1)$$

$$-R_m = 2k_r [\text{Mn}^{3+}] [\text{EAA}]. \quad (2)$$

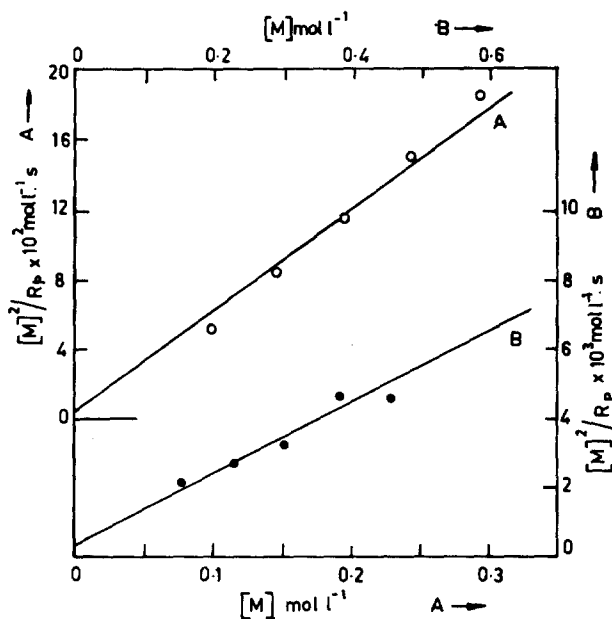
In the polymerization of both the monomers,  $R_p$  is not affected by the variation of  $[\text{Mn}^{3+}]$ . Hence the term  $(k_0/k_i) [\text{Mn}^{3+}]$  is not important in (1). The value of the term  $(k_0/k_i) [\text{Mn}^{3+}]$  is calculated from the plots of  $[\text{M}]^2/R_p$  vs.  $[\text{M}]$  (figures 6A and 6B) and it is found to be 0.007143 for acrylic acid and 0.00937 for methacrylamide. These values are negligibly small when compared to the value of  $[\text{M}]$  in (1). Hence if  $(k_0/k_i) [\text{Mn}^{3+}]$  is neglected, (1) reduces to.

$$R_p = \frac{k_p k_r [\text{EAA}] [\text{M}]}{k_t}, \quad (3)$$

which accounts satisfactorily for the experimental observations.

### 3.4 Evaluation of rate parameters

From the plots of  $-R_m$  vs.  $[\text{Mn}^{3+}]$  (figures 5A and 5B) the second-order rate constant  $k_r$  is evaluated in both the systems. The values of  $k_r$  obtained from polymerization experiments are much less than that observed from oxidation experiments (table 1). This shows that the majority of the primary radicals are utilized for initiation of polymerization.



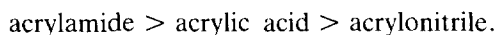
**Figure 6.** (A) Plot of  $[\text{M}]^2/R_p$  vs.  $[\text{M}]$  (for the acrylic acid system) at constant  $\text{EAA} = 5 \times 10^{-3} \text{ M}$ ,  $[\text{Mn}^{3+}] = 2.37 \times 10^{-3} \text{ M}$ ,  $[\text{H}^+] = 2.0 \text{ M}$ ,  $\mu = 2.4 \text{ M}$  and  $T = 35^\circ\text{C}$ . (B) Plot of  $[\text{M}]^2/R_p$  vs.  $[\text{M}]$  (for methacrylamide system) at constant  $[\text{EAA}] = 5 \times 10^{-3} \text{ M}$ ,  $[\text{Mn}^{3+}] = 1.74 \times 10^{-3} \text{ M}$ ,  $[\text{H}^+] = 2.0 \text{ M}$ ,  $\mu = 2.4 \text{ M}$  and  $T = 35^\circ\text{C}$ .

The rate parameters  $k_0/k_i$  and  $k_p/k_t$  are evaluated from the slope and intercept of the plots of  $[M]^2/R_p$  vs.  $[M]$  (figures 6A and 6B) and presented in table 1.

The energy of activation for the overall rate of polymerization is calculated for both the monomers and shown in table 2. The other thermodynamic parameters, viz., the entropy of activation ( $\Delta S^\ddagger$ ) and the free energy of activation ( $\Delta G^\ddagger$ ) for the overall rate of polymerization are also evaluated for both the systems (table 2).

### 3.5 Monomer reactivity

Elayaperumal *et al* (1982) made a comparative study of the reactivities of three vinyl monomers and reported the following order,



In continuation of this study, the monomer reactivities of acrylic acid and methacrylamide are compared in this paper. The ratio  $k_i/k_0$  can be taken as a measure of the relative reactivity of the monomer with the primary radical, since reaction of  $Mn^{3+}$  with the primary radical is common for both the systems in our study. The  $k_i/k_0$  value for acrylic acid (0.332) is greater than that for methacrylamide (0.186). This indicates that acrylic acid has higher monomer reactivity than methacrylamide.

### 3.6 Polymer radical reactivity

When two or more monomers follow the same mechanism under identical reaction conditions, the values of the rate coefficient  $k_p/k_t$  may be considered to be a measure of polymer radical reactivity (Elayaperumal *et al* 1982). Otsu (1971) observed that polymer radical reactivity varies inversely with the  $Q$  values of the monomers. The  $Q$  values of acrylic acid and methacrylamide are 1.15 and 1.46, respectively

**Table 1.** Rate parameters.

Monomer	Temperature (°C)	$k_r \times 10^2 \text{ l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ .				
		From oxidation experiments	From polymeri- sation experi- ments	$k_p/k_t$	$k_0/k_i$	$k_i/k_0$
Acrylic acid	35°	5.607	0.680	5.25	3.01	0.332
Methacryl- amide	35°	5.607	1.041	1.80	5.39	0.186

**Table 2.** Thermodynamic parameters.

Monomer	$\Delta E^\ddagger$ (kcal/mol)	$\Delta S^\ddagger_{308^\circ\text{K}}$ (eu/mol)	$\Delta G^\ddagger$ (kcal/mol)
Acrylic acid	9.35	-50.57	24.90
Methacrylamide	9.55	-49.39	24.76

(Young 1975). Hence the polymer radical reactivity of these two monomers should be in the order,

acrylic acid > methacrylamide.

The  $k_p/k_t$  values obtained at 35°C for acrylic acid and methacrylamide are 5.25 and 1.80, respectively. This shows that the polyacrylic acid radical is more reactive than the polymethacrylamide radical.

Elayaperumal *et al* (1982) observed that vinyl monomers with low  $e$  value afford more reactive polymer radicals and vice versa. The  $e$  values of acrylic acid and methacrylamide are 0.77 and 1.24, respectively (Young 1975). Hence the poly(acrylic acid) radical should be more reactive than the poly(methacrylamide) radical. This is completely in agreement with our observation, viz. that  $k_p/k_t$  (polymer radical reactivity) for acrylic acid is greater than that for methacrylamide.

## References

- Andrulis P J Jr, Dewar M J S, Dietz R and Hunt R L 1966 *J. Am. Chem. Soc.* **88** 5473  
Balakrishnan T and Subbu S 1986 *J. Polym. Sci., Polym. Chem. Ed.* **24** 2271  
Balakrishnan T and Subbu S 1988 *J. Polym. Sci., Polym. Chem. Ed.* (in press)  
Elayaperumal P, Balakrishnan T, Santappa M, and Lenz R W 1979 *J. Polym. Sci., Polym. Chem. Ed.* **17** 4099  
Elayaperumal P, Balakrishnan T, Santappa M and Lenz R W 1980 *J. Polym. Sci., Polym. Chem. Ed.* **18** 2471  
Elayaperumal P, Balakrishnan T, Santappa M and Lenz R W 1982 *J. Polym. Sci., Polym. Chem. Ed.* **20** 3325  
Fuson R C and Wojcik H 1933 *Organic synthesis* (New York: Wiley) pp. 42, 43  
Gangadevi N and Mahadevan V 1972 *Makromol. Chem.* **152** 177  
Gangadevi N and Mahadevan V 1973 *Makromol. Chem.* **166** 209  
Otsu T 1971 *Prog. Polym. Sci., Jpn.* **1** 1  
Young L J 1975 *Polymer handbook* (eds) J Brandrup and E M Immergut (New York: Interscience) pp. II-396 and II-400