Asian Journal of Chemistry Vol. 18, No. 1 (2006), 503–508

Kinetics of Polymerization of Some Vinyl Monomers by Mn(III)-Aspartic Acid Redox System

S. SHANMUGA SUNDARI† and S. SUBBU*
Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India

The polymerization of acrylamide, acrylic acid and methyl acrylate initiated by Mn(III)-aspartic acid redox system in aqueous sulphuric acid has been studied. The influence of [monomer], [Mn(III) ion], [aspartic acid], [H^+] and ionic strength of medium on the rates of polymerization and Mn(III) ion disappearance has been investigated. The effect of temperature on the rate of polymerization has been studied in the range of 298–318 K and the thermodynamic quantities have been evaluated. A suitable mechanism consistent with the kinetic results has been proposed. The rate coefficients (k_i/k_0) of the monomers are calculated and their reactivities are compared.

Key Words: Kinetics, Polymerization, Vinyl monomers, Redox system.

INTRODUCTION

The solution chemistry of Mn(III) ion is of immense interest since trivalent state is one of the unusual oxidation states of manganese. Mn(III) ion coupled with several organic substrates such as diglycolic acid[1], isobutyric acid[2], cyanoacetic acid[3] and lactic acid[4] have been used as efficient redox systems for the initiation of vinyl polymerization. Literature survey revealed that only in a few cases[5, 6] Mn(III)-substrate redox systems were used as initiators in the study of reactivities of vinyl monomers. In this paper we report the results of our kinetic study of polymerization of acrylamide, acrylic acid and methyl acrylate initiated by Mn(III)-aspartic acid redox system. This paper also attempts to compare the reactivities of the three vinyl monomers in homopolymerization.

EXPERIMENTAL

Manganese(III) acetate dihydrate was prepared by the procedure adopted in literature[7]. Acrylamide[8] was purified by recrystallization from chloroform. Acrylic acid[9] was purified by distilling twice over cuprous chloride under pressure (50°C/15 mm). Methyl acrylate was purified by distillation under reduced pressure (20°C/65 mm). Chemicals such as aspartic acid (ASA), sulphuric acid and sodium bisulphate used were of AnalaR grade.

The polymerization experiments were carried out in a reaction tube in nitrogen atmosphere in aqueous sulphuric acid medium. Bromometric method was adopted to follow the rate of polymerization and iodometric method to follow the rate of Mn(III) ion disappearance.

---

†Department of Chemistry, Rajalakshmi Engineering College, Chennai-602 105, India.

RESULTS AND DISCUSSION

Mn(III)-aspartic acid redox initiated polymerization of acrylamide, acrylic acid and methyl acrylate takes place at measurable rates at 35°C. Induction period was not observed in deaerated conditions. The steady state rate of polymerization was reached in 5 min in the polymerization of all the three vinyl monomers.

The rate of polymerization, R_p, varies directly with the concentration of monomer. R_p shows 1.5 order dependence in the case of acrylamide and first order dependence in the case of both acrylic acid and methyl acrylate. The plot of R_p *vs.* $[M]^{1.5}$ was a straight line passing through origin in the case of acrylamide (Fig. 1A). The plots of R_p *vs.* $[M]^1$ were linear with zero intercept (Fig. 1B, 1C) in the case of acrylic acid and methyl acrylate.

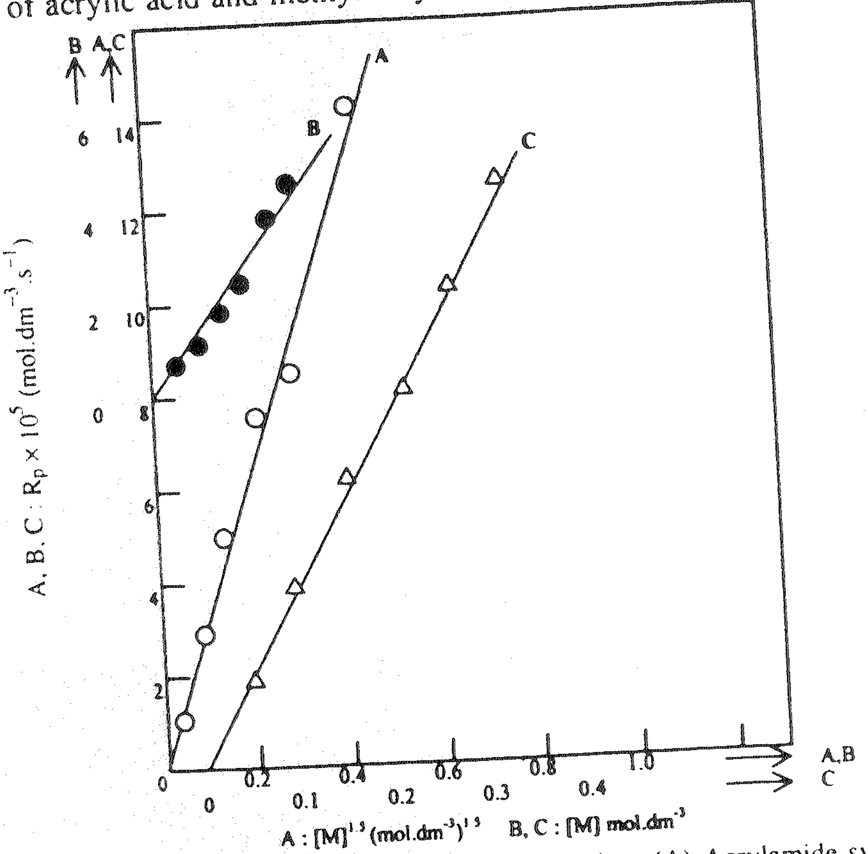


Fig. 1. Mn(III)-aspartic acid-monomer systems, [M] Variation: (A) Acrylamide system, (B) Acrylic acid system, (C) Methylacrylate system

The rate of polymerization shows a 0.5 order dependence on [Mn(III)] and [ASA] each in the polymerization of both acrylamide and acrylic acid (Figs. 2, 3). R_p is observed to be almost independent of [Mn(III)] and [ASA] in the case of methyl acrylate. There is no significant change in R_p with the variation in hydrogen ion concentration and ionic strength of the medium.

The rate of Mn(III) ion disappearance ($-R_m$) was directly proportional to the first power of [M(III)] in all the three monomers. $-R_m$ shows a slight increase with increase in monomer concentration in both acrylamide and methyl acrylate. $-R_m$ remains almost constant with increase in monomer concentration in the case of acrylic acid. $-R_m$ increases uniformly with increase in the concentration of

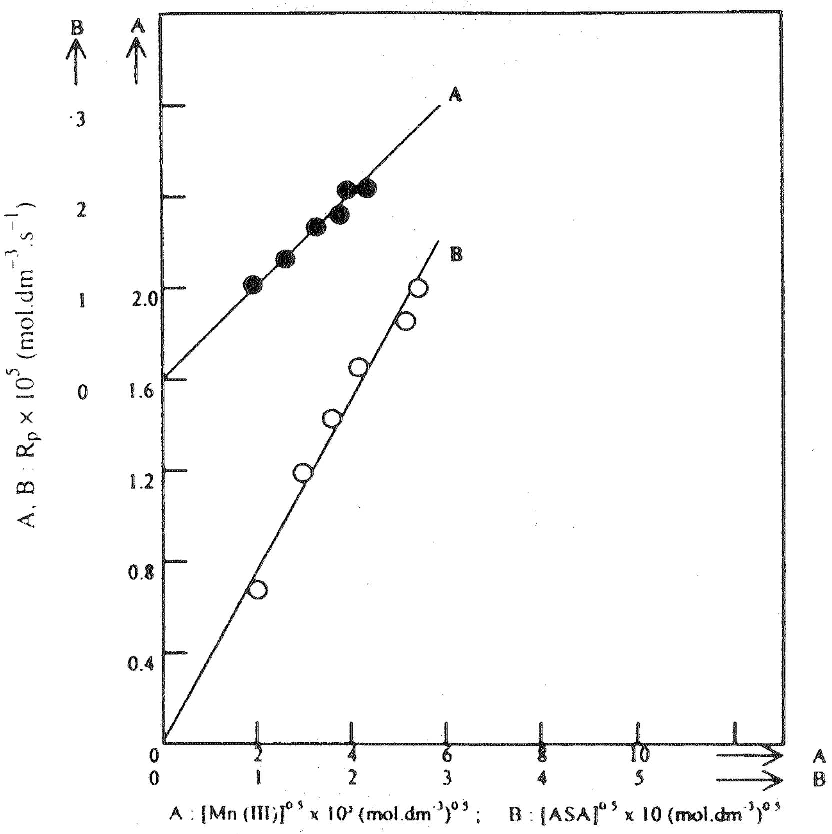


Fig. 2. Mn(III)-aspartic acid-acrylamide system [Mn(III)] and [ASA] variation

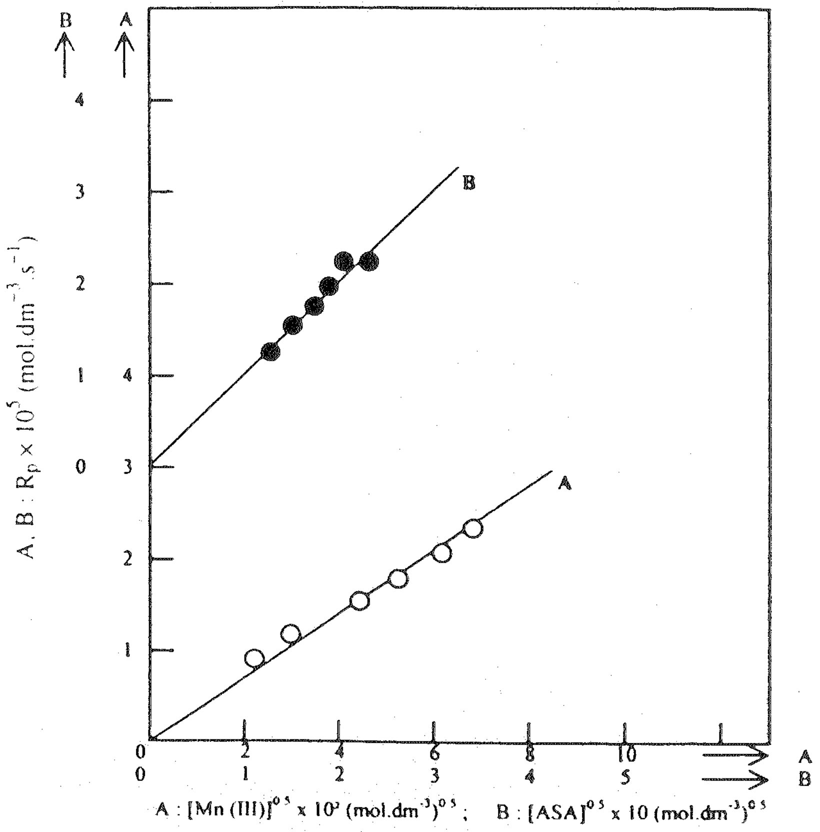


Fig. 3. Mn(III)-aspartic acid-acrylic acid system Mn(III) and [ASA] variation

aspartic acid in the polymerization of acrylamide, acrylic acid and methyl acrylate (Fig. 4). In all the three monomers $-R_m$ remains unaltered by the change in $[H^+]$ and ionic strength of the medium.

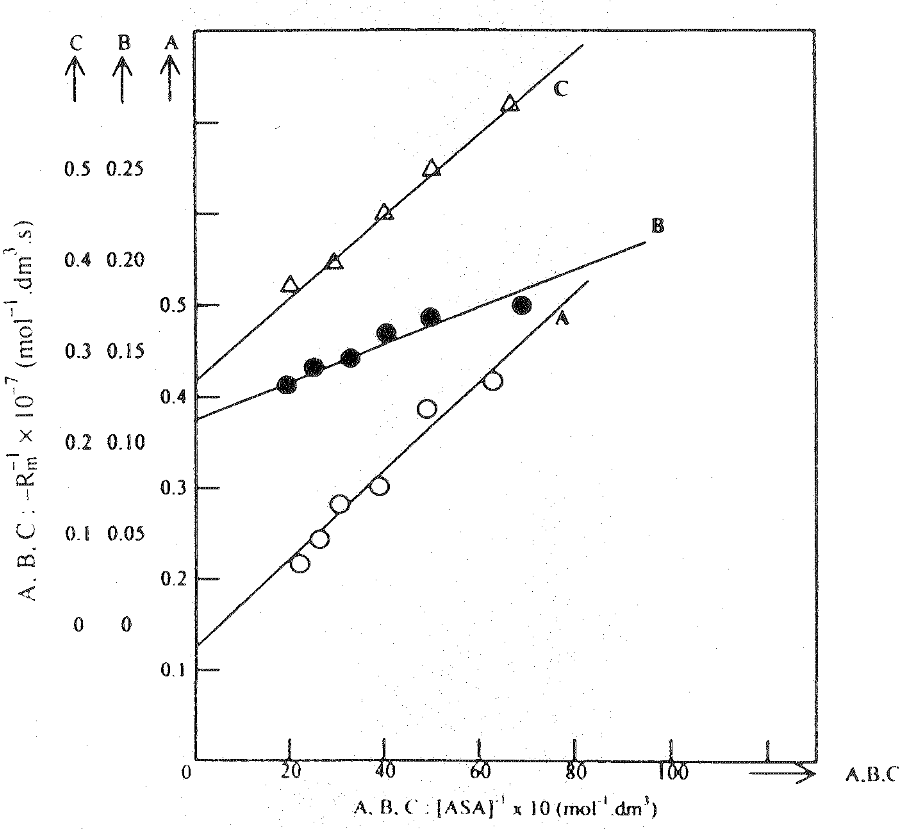
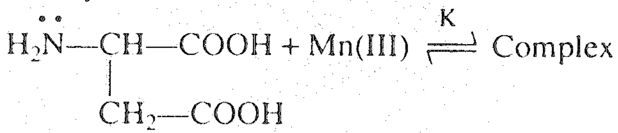


Fig. 4. Mn(III)-aspartic acid-monomer systems $-R_m^{-1}$ *vs.* $[ASA]^{-1}$ Plot: (A) Acrylamide system (B) Acrylic acid system (C) Methylacrylate system

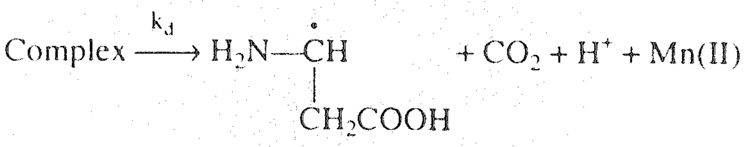
The following reaction scheme has been proposed to explain the above-mentioned kinetic features:

Formation of primary radical (R*)



$$H_2\ddot{N}-\underset{\displaystyle CH_2-COOH}{CH}-COOH + Mn(III) \overset{K}{\rightleftharpoons} Complex$$

(ASA)



$$Complex \xrightarrow{k_d} H_2N-\underset{\displaystyle CH_2COOH}{\dot{C}H} + CO_2 + H^+ + Mn(II)$$

$(R^{\bullet})$

Reaction of primary radical with Mn(III):

$$R^{\bullet} + Mn(III) \xrightarrow{k_0} Products$$

Initiation:

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

where M is the monomer.

Propagation:

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

$$\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$M_{x-1}^{\bullet} + M \xrightarrow{k_p} M_x^{\bullet}$$

where $M_x^{\bullet}$ and $M_{x-1}^{\bullet}$ are polymer radicals.

Termination:

Mutual termination (for acrylamide, acrylic acid)

$$M_x^{\bullet} + M_y^{\bullet} \xrightarrow{k_{t_1}} \text{Polymer}$$

where $M_y^{\bullet}$ is polymer radical.

Complex termination (for methyl acrylate):

$$M_x^{\bullet} + \text{complex} \xrightarrow{k_{t_2}} \text{Polymer} + Z' + \text{Mn(II)} + H^+$$

where Z′ is an inactive product.

The following expressions for R_p and $-R_m$ are arrived at by adopting the stationary state assumption for the free radical concentrations and the principle of non-dependence of rate constants on the chain lengths.

In the case of acrylamide,

$$R_p = k_p M^{3/2} \left(\frac{Kk_d[\text{Mn(III)}][\text{ASA}]}{k_{t_1}([M] + (k_0/k_i)[\text{Mn(III)}])} \right)^{1/2}$$

In the case of acrylic acid,

$$R_p = k_p[M] \left(\frac{Kk_d[\text{Mn(III)}][\text{ASA}]}{k_{t_1}} \right)^{1/2}$$

In the case of methyl acrylate,

$$R_p = \frac{k_p k_d [M]}{k_{t_2}}$$

In the case of acrylamide and acrylic acid,

$$-R_m = \frac{Kk_d[\text{Mn(III)}]_{\text{total}}[\text{ASA}]}{1 + K[\text{ASA}]}$$

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

In the case of methyl acrylate,

$$-R_m = \frac{2Kk_d[\text{Mn(III)}]_{\text{total}}[\text{ASA}]}{1 + K[\text{ASA}]}$$

The second order rate constant k_d has been computed from the plot of $-R_m^{-1}$ *vs.* $[\text{ASA}]^{-1}$. Polymerization experiments gave lower k_d values than oxidation experiments which is indicative of the fact that a major portion of primary radicals are utilized for initiation of polymerization (Table-1).

TABLE-1

Monomer	$\Delta S^{\neq}$ (kJ mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})	$k_d \times 10^4$ dm^3 m^{-1} s^{-1}	
			From oxidation experiment	From polymerization experiment
Acrylamide	−177.69	102.59	4.562	4.189
Acrylic acid	−166.02	102.88	4.562	2.090
Methyl acrylate	−194.51	102.42	4.562	2.064

Comparison of Monomer Reactivity

Since oxidation step is common for all the three monomers, the value of k_i/k_0 may be taken as a measure of the monomer reactivity.

The k_i/k_0 value of methyl acrylate (0.2597) is higher than those of acrylamide (0.2247) and acrylic acid (0.1367). This shows that methyl acrylate is more reactive than acrylamide and acrylic acid towards Mn(III)-ASA redox system. Thus, the monomer reactivities of the three vinyl monomers are in the order

methyl acrylate > acrylamide > acrylic acid

A review of the R_p values and the activation energies of the three vinyl monomers (Table-2) also confirm this order.

TABLE-2

Monomer	Methyl acrylate	Acrylamide	Acrylic acid
k_i/k_0	0.2597	0.2247	0.1367
$R_p \times 10^5$ (mol dm^{-3} s^{-1})	10.2600	5.0500	4.7900
E_a (kJ mol^{-1})	42.5100	47.8600	51.7600

REFERENCES

1. P. Elayaperumal, T. Balakrishnan, M. Santappa and R.W. Lenz, *J. Polym. Sci.*, **17**, 4099 (1979).
2. ———, *J. Polym. Sci.*, **18**, 2471 (1980).
3. Mahadevan and Venkatanarayanan, *Macromol. Chem. Phys.*, **197**, 367 (1996).
4. K. Mohana, K.R. Chandra and T. Raju, *Macromol New Front, Proc. IUPAC Int. Symp. Adv. Polym. Sci. Tech.*, **1**, 171 (1998).
5. P. Elayaperumal, T. Balakrishnan, M. Santappa and R.W. Lenz, *J. Polym. Sci.*, **20**, 3325 (1982).
6. T. Balakrishnan and S. Subbu, *Proc. Indian Acad. Sci., Chem. Sci.*, **100**, 469 (1988).
7. P.J. Andrulis (Jr.), M.J.S. Dewar, R. Dietz and R.L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).
8. F.S. Dainton and M. Tordoff, *Trans. Faraday Soc.*, **53**, 499 (1957).
9. T. O'Neil, *J. Polym. Sci.*, **10A-1**, 569 (1972).

(*Received*: 21 March 2005; *Accepted*: 3 October 2005) AJC-4431