European Polymer Journal, Vol. 14, pp. 287 to 290.

0014-3057/78/0501-0287 $02.00/0

AQUEOUS POLYMERIZATION OF ACRYLONITRILE INITIATED BY THE Mn^{3+}/CITRIC ACID REDOX SYSTEM

Padma L. Nayak,* Rajani K. Samal and Mohan C. Nayak
Department of Polymer Chemistry, Ravenshaw College, Cuttack-753003 India

(*Received* 3 *November* 1976; *revised* 19 *July* 1977)

Abstract—Kinetics of polymerization of acrylonitrile initiated by the redox system Mn^{3+}/citric acid were investigated in aqueous sulphuric acid in the range of 20–25°; initial rates of polymerization and Mn^{3+} disappearance etc. were measured. The effects of certain water miscible organic solvents and certain cationic and anionic detergents on the rate of polymerization have been examined. A mechanism has been suggested involving formation of a complex between Mn^{3+} and citric acid, decomposition of which yields the initiating free radical and with polymerization being terminated by mutual interaction of growing radicals.

INTRODUCTION

In a series of papers Waters *et al.* [1–3] have reported that dibasic acids, e.g. malonic acid, can be oxidized by manganic pyrophosphate and manganic sulphate through a free radical mechanism. Singh *et al.* [3] and Namasivayam *et al.* [4] have reported that manganic sulphate in excess sulphuric acid may form an effective redox system for grafting of polymethyl methacrylate on cellulose and polyvinyl alcohol. Nayudamma *et al.* [5] have reported manganese-(III)-initiated graft copolymerization of vinyl monomers onto collagen. In this laboratory, there is a research programme to use trivalent manganese, in either the form of pyrophosphate or sulphate for grafting vinyl monomers onto wool, silk, cotton etc. We have reported the aqueous polymerization of acrylonitrile [6–9], methyl acrylate and methyl methacrylate [10] using quinquevalent vanadium and many organic substrates. This communication reports on studies of polymerization of acrylonitrile (AN) initiated by the redox system Mn^{3+}–citric acid. From the experimental observations, a reaction scheme is suggested and the various kinetic parameters evaluated.

EXPERIMENTAL

Acrylonitrile (Nakarai Chemicals Ltd., Japan) was washed with 5% NaOH, dilute H_3PO_4 and finally with water and dried over anhydrous $CaCl_2 \cdot$Mn(II) sulphate was an EM-GR product. All other reagents were AR grade. Citric acid (CA), AR was crystallized several times before use. Manganese(III) stock solutions were prepared by electrolytic oxidation of the appropriate Mn^{2+} salt solution (0.4–0.6 M) in 4–6 M sulphuric acid, at a platinum anode [11, 12]. Freshly prepared solutions which were immediately used were analysed for Mn^{3+} by cerimetry, and for the total manganese content by EDTA titration [13]. Water distilled thrice over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U.K.) was used to prepare all solutions. Nitrogen for de-aeration of experimental systems was purified by passing through several columns of Fieser's solution, a column of saturated lead acetate solution, and finally a wash bottle, containing distilled water.

The polymerizations were heterogeneous, with polymer precipitating continuously. Rates of polymerization were obtained gravimetrically; rates of oxidant consumption were obtained by cerimetry on reaction mixtures arrested by addition of excess standard ferrous sulphate solution. Polymers were dissolved in dimethylformamide and reprecipitated in cold methanol.

RESULTS AND DISCUSSION

Acrylonitrile was polymerized in aqueous solutions at 20 and 25° in sulphuric acid and in the presence of the redox system: manganese(III) sulphate–citric acid. Typical time-conversion curves for 25° at various citric acid concentrations (0.5×10^{-3}–4×10^{-3} M) at constant [Mn^{3+}] (1.75×10^{-3} M] are shown in Fig. 1. Acrylonitrile was also polymerized under conditions identical to those mentioned above, with Mn^{3+} in the presence of other carboxylic acids viz. tartaric acid, ascorbic acid, oxalic

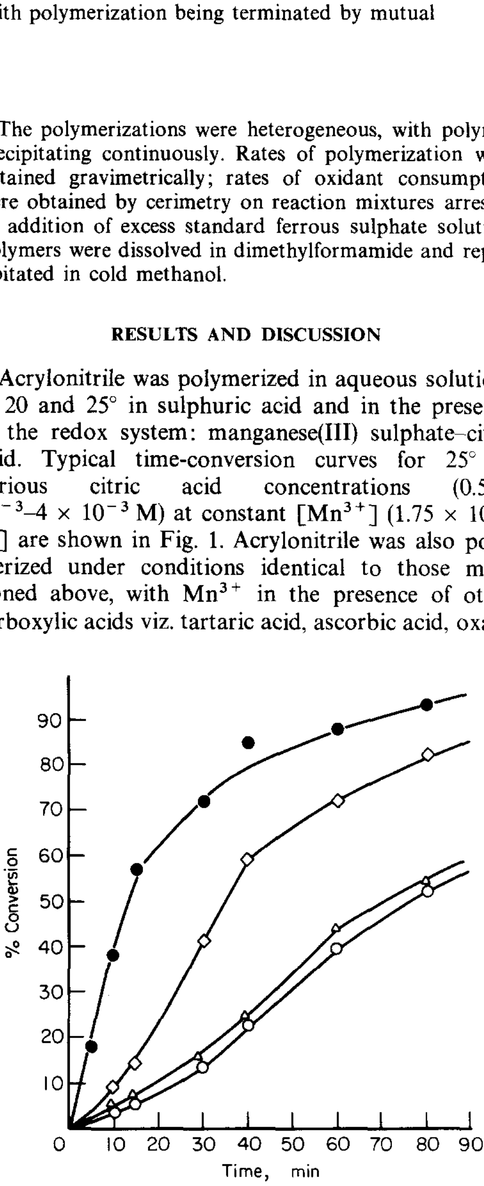

Fig. 1. Plots of conversion % vs time. [Mn(III)] = 1.75 $\times 10^{-3}$ M. [H^+] = 1.425 M, μ = 1.5095 M, [M] = 0.7539 M, Temp = 25°. (○): [CA] = 0.5×10^{-3} M, (△): [CA] = 1.5×10^{-3} M, (◇): [CA] = 3.0×10^{-3} M, (●): [CA] = 4.0×10^{-3} M.

---

* To whom all correspondence should be addressed.

Table 1. Polymerization of acrylonitrile by various Mn^{3+}-carboxylic acid systems at 20°

Acid	Concentration	Induction period (min)	Initial rate $R_p \times 10^5$ (mole/l-sec.)
Citric acid	3×10^{-3} M	2	12.05
Tartaric acid	3×10^{-3} M	8	2.83
Ascorbic acid	3×10^{-3} M	nil	0.7452
Oxalic acid	3×10^{-3} M	3	0.5047
Succinic acid	3×10^{-3} M	15	0.3254
Glutaric acid	3×10^{-3} M	40	0.2825
Adipic acid	3×10^{-3} M	60	0.2157

Reaction conditions: $[Mn^{3+}] = 1.75 \times 10^{-3}$ M. $[H_2SO_4] = 1.83$ M. [AN] = 0.7539 M. $\mu = 1.957$ M.

acid, succinic acid, glutaric acid and adipic acid. Results reported in Table 1 show that, under identical conditions, the order of reactivity of the acids is Citric > tartaric > ascorbic > oxalic > succinic > glutaric > adipic.

The rate of manganic ion disappearance $(-d[Mn^{3+}]/dt)$ was proportional to $[Mn^{3+}]$ (Fig. 2) but independent of [monomer]. Plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs $[CA]^{-1}$ were linear with the intercept on the rate axis (Fig. 3) showing Michaelis–Menten [14] or Lineweaver and Burk [15] kinetics for complex formation. Similar complex formation by malonic acid and manganese(III) has been reported by Waters and Colleagues [2]. The reaction is catalysed by both sulphuric and perchloric acids. The initial rates increased with [CA]; plots of reciprocal rates vs $[CA]^{-1}$ were linear with intercepts on the rate axis (Fig. 3).

The plots of R_p versus $[M]^{3/2}$ were linear and passed through the origin (Fig. 4); therefore the order with respect to [M] was 1.5. The initial rate of polymerization, R_p, was directly proportional to $[Mn^{3+}]$. The initial rate of polymerization is proportional to $[\text{citric acid}]^{\frac{1}{2}}$ (Fig. 3).

Effect of water-miscible organic solvents

Water miscible organic solvents are found to depress considerably the rate of polymerization as well the maximum conversion. Solvents such as ethanol, methanol etc. decrease the area of shielding of a strong hydration layer in aqueous medium resulting in the termination of the radical end of the growing chains; these solvents increase the regulated rate of production of primary radicals; under the existing experimental conditions, this effect renders the termination relatively fast as compared with the growth of the poymer chains as pointed out by Kern *et al.* [16]. Palit *et al.* [17] have made similar observation even for the homogeneous polymerization in non-aqueous medium in which water is the additive.

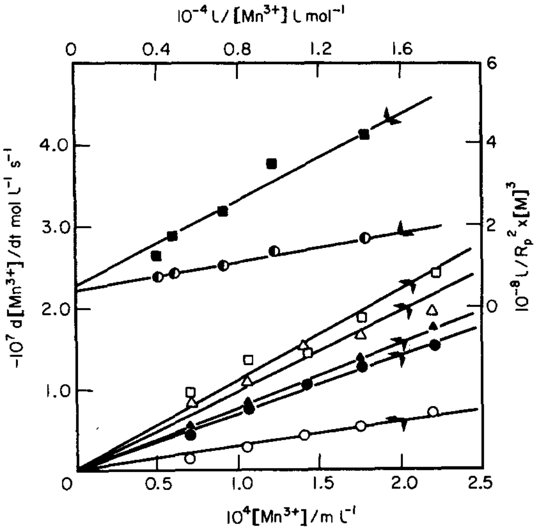

Fig. 2. (a) Plots of $-d[Mn(III)]/dt$ vs [Mn(III)], $[H^+] = 1.83$ M, $\mu = 1.957$ M, [AN] = 0.305 M, (○): Temp = 20°, [CA] = 2×10^{-3} M, (△): Temp = 25°, [CA] = 2×10^{-3} M, (□): Temp = 25°, [CA] = 2.5×10^{-3} M, (●): Temp = 20°, [CA] = 2.5×10^{-3} M, (▲): Temp = 20°, [CA] = 3.8×10^{-3} M. (b) Plots of $1/R_p^2[M]^3$ vs 1/[Mn(III)], [CA] = 2.0×10^{-3} M, $[H^+] = 1.83$ M, $\mu = 1.957$ M, [M] = 0.6031 M. (◐); Temp = 25°, (■): Temp = 20°.

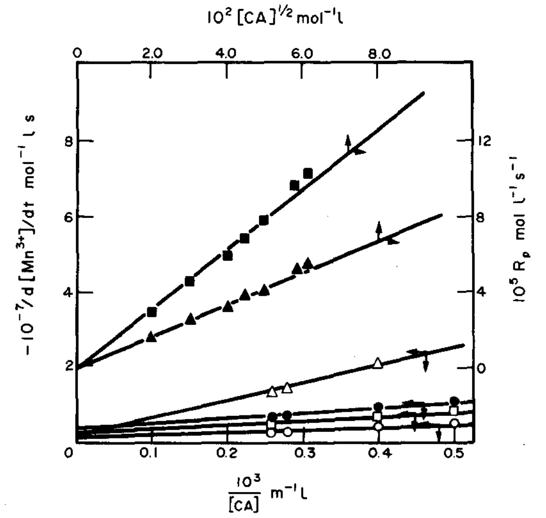

Fig. 3. (a) Plots of 1/d [Mn(III)]/dt vs 1/[CA], $[H^+] = 1.83$ M, $\mu = 1.957$ M, [M] = 0.3015 M. (○): Temp = 25°, [Mn(III)] = 2.45×10^{-3} M, (□): Temp = 25°, [Mn(III)] = 1.05×10^{-3} M, (●): Temp = 25° [Mn(III)] = 0.70×10^{-3} M, (△): Temp = 20° [Mn(III)] = 0.70×10^{-3} M. (b) Plots of R_p vs $[CA]^{1/2}$, [Mn(III)] = 1.05×10^{-3} M, $[H^+] = 1.83$ M, $\mu = 1.957$ M, [AN] = 0.6031 M, (▲): Temp = 20° (■): Temp = 25°.

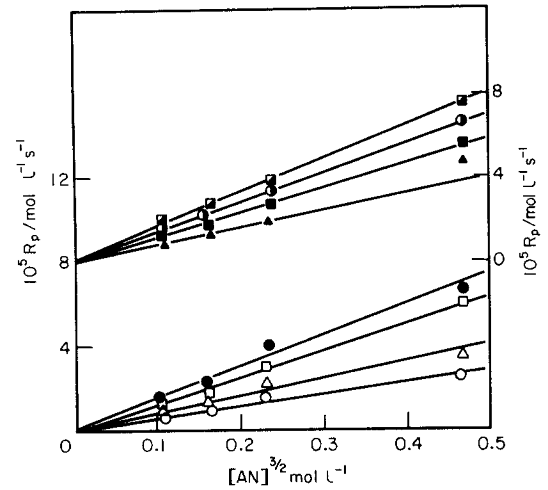

Fig. 4. Plots of R_p vs $[M]^{3/2}$, $[CA] = 2.0 \times 10^{-3}$ M, $[H^+] = 1.83$ M. $\mu = 1.957$ M. (a) Temp = 20°. (○): [Mn(III)] = 0.7×10^{-3} M, (△): [Mn(III)] = 1.05×10^{-3} M, (□): [Mn(III)] = 1.75×10^{-3} M, (●): [Mn(III)] = 2.5×10^{-3} M. (b) Temp = 25°. (▲): [Mn(III)] = 0.7×10^{-3} M, (■): [Mn(III)] = 1.05×10^{-3} M, (◑): [Mn(III)] = 1.75×10^{-3} M, (◪): [Mn(III)] = 2.45×10^{-3} M.

Effect of surfactants

The polymerization has been investigated in presence of micelles of certain cationic, anionic and non-ionic surfactants. Cationic micelles of cetyl trimethylammonium bromide (CTABr) retard the process while anionic micelles of sodium lauryl sulphate (NaLS) accelerate it and a non-ionic surfactant Triton X-100 has no effect. Catalysis of the polymerization by NaLS can be explained on the assumption that the organic substrate when incorporated by the anionic micelles of NaLS, is in an electrostatic environment [18–20] favourable for attack by the tripositive manganese ion; hence the formation of free radical becomes easier and the polymerization rate increases. The retardation of the reaction in the micelles of cationic nature may be explained in terms of incorporation of the substrate into the cationic micelle where it is shielded electrostatically from attack by Mn^{3+}.

Reaction mechanism and rate law

The polymerization of acrylonitrile in aqueous media initiated by Mn^{3+} in the presence of citric acid shows characteristic features of heterogeneous polymerization. The reaction system becomes heterogeneous as soon as polymerization starts, due to insolubility of the polymer.

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme is suggested involving initiation by an organic free radical produced by the interaction of Mn^{3+} with citric acid and termination by mutual combination

$$Mn^{3+} + CA \xrightleftharpoons{K_1} \text{Complex} \tag{1}$$

$$\text{Complex} \xrightarrow{k_r} R^{\cdot} + Mn^{2+} + H^+ \tag{2}$$

$$R^{\cdot} + Mn^{3+} \xrightarrow{k_0} Mn^{2+} + \text{products} \tag{3}$$

$$R^{\cdot} + M \xrightarrow{k_i} R - M^{\cdot} \tag{4}$$

$$RM^{\cdot} + M \xrightarrow{k_p} RM_2^{\cdot} \tag{5}$$

$$RMn^{\cdot} + RM_m^{\cdot} \xrightarrow{k_t} \text{Polymer} \tag{6}$$

Applying the steady state principle to the primary radical $R^{\cdot}$ as well as to the growing radical $RM\dot{n}$ and making the usual assumption that radical reactivity is independent of radical size, we obtain the following rate expressions:

$$\frac{-d[Mn^{3+}]}{dt} = k_r K_1 [Mn^{3+}][CA] + \frac{k_0 k_r K_1 [Mn^{3+}]^2 [CA]}{(k_0[Mn^{3+}] + k_i[M])}. \tag{7}$$

The second term in Eqn (7) is due to reaction (3). If $k_0[Mn^3] \gg k_i[M]$, this term is reduced to:

$$\frac{-d[Mn^{3+}]}{dt} = 2k_r K_1 [Mn^{3+}][CA]. \tag{8}$$

Since the measured rate $-d[Mn^{3+}]/dt$ applies to the total $[Mn^{3+}]$ regardless of the species and since

$$[Mn^{3+}]_T = [Mn^{3+}] \times (1 + K_1[CA]),$$

we obtain

$$-d[Mn^{3+}]/dt = \frac{2k_r K_1 [Mn^{3+}]_T [CA]}{(1 + K_1[CA])}. \tag{9}$$

The polymerization rates are given by

(for $k_p[RM^{\cdot}] \gg k_i[R^{\cdot}]$)

$$-d[M]/dt = \frac{k_p k_i^{1/2} (k_r K_1 [Mn^{3+}][CA])^{1/2} [M]^{3/2}}{k_t^{1/2} (k_0[Mn^{3+}] + k_i[M])^{1/2}}.$$

If $k_0[Mn^{3+}] \gg k_i[M]$ Eqn (10) reduces to

(10)

$$\frac{-d[M]}{dt} = \frac{k_p k_i^{1/2} (k_r K_1 [CA])^{1/2} [M]^{3/2}}{k_0^{1/2} \cdot k_t^{1/2}}. \tag{11}$$

Now Eqn (10) can be rearranged to

$$\frac{(-d[M])^{-2}}{dt} = \frac{k_t k_0}{k_p^2 k_i k_r K_1 [CA][M]^3} + \frac{k_t}{k_p^2 k_r K_1 [Mn^{3+}]_T [CA][M]^2} + \frac{k_t}{k_p^2 k_r [Mn^{3+}]_T [M]^2}. \tag{12}$$

The plots of $-([M]/dt)$ vs $[CA]^{-1}$ are linear with intercepts on the ordinate (Fig. 6).

Evaluation of K_1, k_r, $k_p/k_t^{1/2}$ and k_0/k_i

The value of K_1 and k_r were computed by plotting $(-d[Mn^{3+}]/dt)^{-1}$ vs $[CA]^{-1}$ (Fig. 3). From the intercepts and the ratio intercept/slope of these plots, the rate of unimolecular decomposition of the complex (k_r) and its formation complex (K_1) can be calculated (see Table 2). Further, according to Eqn (12), the plots of $(-d[M]/dt)^{-2}$ vs $[CA]^{-1}$ are linear with intercepts on the ordinate (Fig. 5). From the intercepts of these plots, we can calculate the ratio $k_p/k_t^{\frac{1}{2}}$. Equation (12) also required that the plots of

Table 2. Values of rate parameters in polymerization of acrylonitrile (AN) initiated by the system citric acid–Mn^{3+}

Temp. (°C)	$10^3 \times k_r$ (sec^{-1})	$10^{-3} K_1$ ($l\,mole^{-1}$)	$k_p/k_t^{1/2} \times 10^{-2}$ ($l^{\frac{1}{2}}\,mole^{-\frac{1}{2}}\,sec^{\frac{1}{2}}$)	$k_0/k_i \times 10^{-2}$
20	4.62	4.4	5.52	6.7
25	6.3	15.0	9.14	7.56

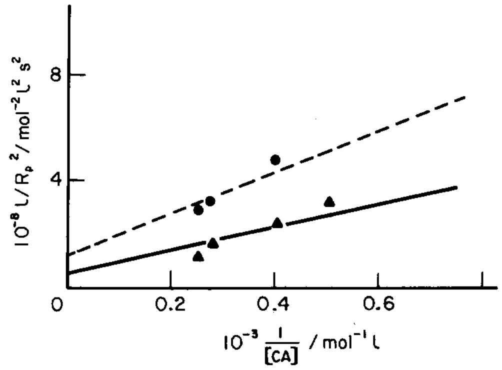

Fig. 5. Plots of $1/R_p^2$ vs $1/[CA]$, $[Mn(III)] = 1.05 \times 10^{-3}$ M, $[H^+] = 1.83$ M, $\mu = 1.957$ M. $[M] = 0.6031$ M. (▲): Temp = 25°, (●): Temp = 20°.

$(-d[M]/dt)^{-2}\ [M]^3$ vs $([Mn^{3+}])^{-1}$ are linear with intercepts equal to $k_t k_0/k_p^2 k_i k_r K_1$ [CA] (Fig. 2b). Using the values of k_p/k_t, the ratio k_0/k_i can be calculated from these intercepts. The values of $k_p/k_t^{1/2}$ and k_0/k_i are reported in Table 2.

In recent years, we have tried to derive rate expressions for the heterogeneous polymerization of vinyl monomers using many metal ions [6–8]. The rate parameters calculated in all these systems differ considerably for different metal ions. This might be due to the difference in oxidation potential of the metal ions in their higher valence states. Recently we reported the homogeneous polymerization of acrylamide using some metal ions [22]. We find that the values of rate parameters are not exactly the same as for heterophase systems, perhaps because of difference in termination of the growing polymer radicals in the two systems.

Acknowledgements—The authors thank Prof. M. Santappa (Director, Central Leather Research Institute, Madras) for many valuable discussions and C.S.I.R. for a Fellowship to one of them (RKS).

REFERENCES

1. A. Y. Drummond and W. A. Waters, *J. chem. Soc.* 2456 (1954).
2. T. J. Kemp and W. A. Waters, *J. chem. Soc.* 1489, 3101 (1964).
3. H. Singh, R. T. Thampy and V. B. Chipalkatti, *J. Polym. Sci.* **A-3**, 1247, 4289 (1965).
4. D. Namasivayam, B. K. Pattnaik and R. T. Thampy, *Makromolek. Chem.* **105**, 144 (1967).
5. K. Satish Babu, K. Panduranga Rao, K. Thomas Joseph, M. Santappa and N. Nayudamma, *Leather Sci.* **21**, 261 (1974).
6. T. R. Mohanty, B. C. Singh and P. L. Nayak, *Makromolek. Chem.* **175**, 2345 (1974).
7. T. R. Mohanty, B. C. Singh and P. L. Nayak, *J. Polym. Sci. Polym. Chem. Ed.* **13**, 2075 (1975).
8. B. C. Singh, T. R. Mohanty and P. L. Nayak, *J. Macromolec. Sci. Chem.*, **A9(7)**, 1149 (1975).
9. B. C. Singh, T. R. Mohanty and P. L. Nayak, *Europ. Polym. J.* **12**, 371 (1976).
10. P. L. Nayak, B. C. Singh and T. R. Mohanty, *Makromolek. Chem.* **176**, 873 (1975).
11. R. G. Selim and J. J. Lingane, *Anal. Chim. Acta.* **21**, 536 (1959).
12. C. F. Wells and C. Davies, *Nature, Lond.* **205**, 692–693 (1965).
13. A. I. Vogel, *Quantitative Inorganic Analysis*, 2nd Edn. Longmans, London (1962).
14. L. Miichaelis and M. L. Menten, *Biochem. Z.* **49**, 333 (1912).
15. H. Lineweaver and D. Burk, *J. Am. chem. Soc.* **56**, 658 (1934).
16. R. Schulz, G. Renner, A. Henglein and W. Kern, *Makromolek. Chem.* **12**, 20 (1954).
17. R. S. Konar and S. R. Palit, *J. Indian. chem. Soc.* **38**, 481 (1961).
18. J. M. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Chemistry*, Academic Press, New York (1975).
19. E. H. Cordes, *Reaction Kinetics in Miçelles*. Plenum Press, New York (1973).
20. E. H. Cordes and R. B. Dunpap, *Accounts. Chem. Res.* **2**, 329 (1969).
21. F. S. Dainton and R. S. Eaton, *J. Polym. Sci.* **39**, 313 (1959).
22. P. L. Nayak, T. R. Mohanty and R. K. Samal, *Macromolecules* **10**, 489–492 (1977).