Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Nayak, Padma L. , Samal, Wani K. and Nayak, Mohan C.(1978) 'Polymerization of Acrylonitrile Initiated by the Thiourea-Mn^3 Redox System', Journal of Macromolecular Science, Part A, 12: 6, 827 — 836

To link to this Article: DOI: 10.1080/00222337808063170

URL: http://dx.doi.org/10.1080/00222337808063170

J. MACROMOL. SCI.–CHEM., A12(6), pp. 827-836 (1978)

Polymerization of Acrylonitrile Initiated by the Thiourea-Mn^{3+} Redox System

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ABSTRACT

Kinetics of vinyl polymerization initiated by the redox system thiourea-Mn^{3+} were investigated in the temperature range 30-40°C in sulfuric acid, and the rates of polymerization R_p and disappearance of Mn^{3+} have been measured. The effect of certain water-miscible organic solvents and anionic surfactant on the rates of polymerization was investigated. A mechanism involving the formation of a complex between Mn^{3+} and thiourea whose decomposition yields the initiating free radical with the polymerization terminated by mutual intraction of growing radicals is suggested.

INTRODUCTION

The use of thioureas and N-substituted thioureas as redox components for initiation of aqueous vinyl polymerization has attracted

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attention in recent years. Bonvicini and Caldo [1] and Sugimura et al. [2, 3] used these reducing agents with hydrogen peroxide as the oxidant for initiation in the aqueous polymerization of acrylonitrile. Delzenne et al. [4] concluded from results of a dye (eosin)-sensitized aqueous photopolymerization of acrylamide in an oxygen atmosphere that the initiating redox system actually consists of thiourea and H_2O_2. Mukherjee et al. [5] used thiourea as reductant with a number of oxidants such as ferric chloride (Fe^{3+}), ethylene dibiguanide complex salts of tripositive silver (Ag^{3+}), hydrogen peroxide, persulfate, and bromate plus hydrochloric acid for initiation of aqueous polymerization of methyl methacrylate. Palit et al. [6] reported the general features and kinetics of vinyl polymerization with Fe(III)-thiourea as initiator system. Shukla and Mishra [7] reported the aqueous polymerization of acrylamide initiated by acidified permanganate and thiourea redox system. Mishra and Gupta [8] reported the aqueous polymerization of methacrylamide initiated by the acidified bromate-thiourea redox system. Recently [9, 10] we reported the aqueous polymerization of acrylonitrile initiated by V^{5+}-thiourea and Cr^{6+}-thiourea redox systems. These redox systems have been found to be quite effective in initiating vinyl polymerization.

In this laboratory, there is a research program under way to investigate the graft copolymerization of vinyl monomers on wool, silk, collagen, and nylon 6 by using these redox systems. We have reported the aqueous polymerization of acrylonitrile, methyl acrylate, methyl methacrylate, and acrylamide with a number of redox systems [11-16]. As a part of the research program, we wish to report the aqueous polymerization of acrylonitrile initiated by the Mn^{3+}-thiourea redox system.

EXPERIMENTAL

Acrylonitrile from Koch-Light Laboratories Ltd. was purified by the method of Bamford et al. [17]. $MnSO_4 \cdot 4H_2O$ was an E. Merck GR product. All other reagents, e. g., thiourea, ferrous ammonium sulfate, and o-phenanthroline, were of AR Grade. Mn(III) stock solutions were prepared by electrolytic oxidation of an appropriate Mn^{2+} salt solution (0.4-0.6 $\underline{M}$) in the 4-6 $\underline{M}$ sulfuric acid at a platinum anode [18, 19]. Freshly prepared solutions, which were used immediately were analyzed for Mn^{3+} content by cerimetry and for total Mn^{3+} content by EDTA titration. Water to prepare all solutions was triply used distilled over alkaline permanganate and deionized by passage through a column of Biodeminrolit resin (Permutit Co., U. K.). Nitrogen used for deaeration of the experimental systems was purified by passage through several columns of Fieser's solution and finally a wash bottle containing distilled water. The polymerization reactions were heterogeneous with the polymer precipitating continuously. Rates of polymerization (initial rates) were obtained gravimetrically, while the rate of oxidant consumption was obtained by cerimetry of reaction mixtures arrested by addition of excess ferrous ammonium sulfate solution. The ionic strength (μ) was maintained by adding the required amount of $NaHSO_4$.

RESULTS AND DISCUSSION

Acrylonitrile was polymerized in aqueous solution at 30-45°C in sulfuric acid in the presence of the Mn^{3+}-thiourea redox system. A typical set of time-conversion curves at 35°C at various thiourea concentrations ($0.125 - 1 \times 10^{-3}$ $\underline{M}$) and at different temperatures (30-40°C) for particular thiourea (0.5×10^{-3} $\underline{M}$) and Mn^{3+} (7×10^{-3} $\underline{M}$) concentrations are shown in Fig. 1. The results in Fig. 1 indicate that the percentage of conversion is increased both by increasing the thiourea concentration and temperature.

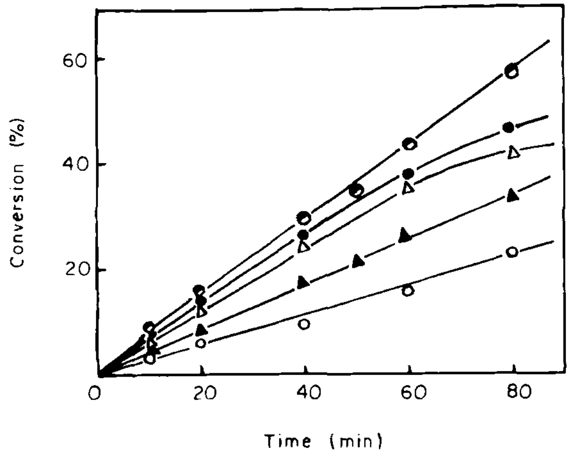

FIG. 1. Plots of conversion vs. time (○, ●, △) at different activator concentrations at 35°C: (○) [TU] = 0.125×10^{-3} $\underline{M}$, (△) [TU] = 0.25×10^{-3} $\underline{M}$, and (●) [TU] = 1×10^{-3} $\underline{M}$; [Mn^{3+}] = 7×10^{-3} $\underline{M}$, [H^+] = 0.85 $\underline{M}$, μ = 1 $\underline{M}$, [AN] = 0.754 $\underline{M}$. Temp = 35°C, and conversion vs. time at constant activator concentration ([TU] = 0.5×10^{-3} $\underline{M}$) at various temperatures: (▲) 30°C, (◐) 40°C. [Mn^{3+}] = 7×10^{-3} $\underline{M}$, [H^+] = 0.85 $\underline{M}$, μ = 1 $\underline{M}$, [AN] = 0.754 $\underline{M}$.

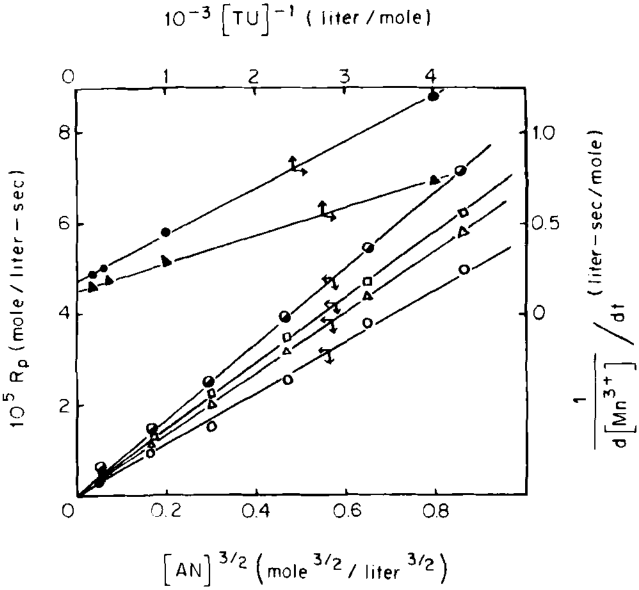

FIG. 2. (a): Plot of R_p vs. $[AN]^{3/2}$ at $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $\mu = 1$ M, $[TU] = 1 \times 10^{-3}$ M: (○) 30°C, (△) 35°C, (□) 40°C, and (◕) 45°C; and plots of $(-d[Mn^{3+}]/dt)^{-1}$ vs. $[TU]^{-1}$ at $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $\mu = 1$ M, $[AN] = 0.754$ M: (●) 30°C and (▲) 40°C.

Rate of Polymerization R_p

The rate of polymerization increased linearly with increasing monomer concentration (0.1508-0.949 M). The plots of R_p versus $[AN]^{3/2}$ were linear and passed through the origin (Fig. 2); therefore, the order with respect to monomer was 3/2. The rate is also increased with the increase of activator (thiourea) concentrations in the range 0.25 - 4 × 10^{-3} M. Further, the plots of the square of the reciprocal rate ($1/R_p^2$) versus the reciprocal of the activator concentration (1/[TU]) were linear with intercept on the rate axis (Fig. 3).

Rate of Disappearance of Manganic Ion

The rates of disappearance of manganic ion, -d[Mn(III)]/dt, were first-order in [Mn(III)] and independent of monomer concentration.

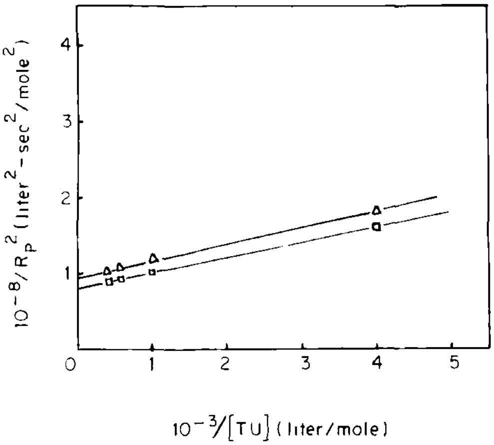

FIG. 3. Plot of $1/R_p^2$ vs. $[1/TU]$: (△) 35°C; (□) 40°C. $[Mn^{3+}] = 7 \times 10^{-3}$ M, $[H^+] = 0.85$ M, $\mu = 1$ M, $[AN] = 0.754$ M.

Plots of $(-d[Mn(III)]/dt)^{-1}$ versus $[TU]^{-1}$ were linear (Fig. 2) with the intercept on the rate axis showing Lineweaver-Burk kinetics for complex formation [20].

Effect of Water-Miscible Organic Solvents

Addition of 5% (v/v) water-miscible organic solvents such as methanol, ethanol, acetone, and acetic acid are found to depress the rate of polymerization as well as the maximum conversion considerably. The retardation of the rate by the solvents might be due to the following reasons. Solvent molecules might decrease the area of shielding of the strong hydration layer in aqueous medium resulting in the termination of the radical end of the growing chain. Further, these solvents might increase the regulated rate of production of primary radicals which under the existing experimental conditions renders the termination rate relatively fast as compared to the rate of growth of the polymer chain. This is in agreement with the views of Kern and co-workers [21]. Also, the interchain hydrogen bonding interlocking the polymer chain is not rigid (strong), and as a result the tendency of mutual termination of the polymer chain increases. Similar observations have been noted by Nayak and co-workers in case of the aqueous polymerization of acrylamide [16].

Effect of Surfactants

In recent years micellar catalysis has played an important role in the kinetics and mechanism of certain polymerization reactions [22-24]. The hydrophobic interactions and electrostatic attractions are mainly responsible for the spectacular rate enhancement or inhibition exhibited by the micelles on the polymerization reactions. Addition of anionic surfactant sodium laurylsulfate to the reaction mixture below and above the critical micelle concentration (CMC) decreased the rate of polymerization. The retarding effect of anions may be explained by assuming specific ion-pair binding of the cation Mn^{3+} with the anion RSO_4^-, which might be lowering the rate of primary radical generation. Alexander and co-workers [23] have assumed such ion-pair binding between cationics and $S_2O_8^{2-}$ ions only above the CMC, leading to the formation of an insoluble complex, which could be dissolved or dispersed by further addition of cationics and a resultant reduction in rate. As expected, the rate of polymerization is not affected in presence of micelles of nonionic surfactants such as Triton X-100.

Reaction Mechanism and Rate Law

The thermal polymerization of acrylonitrile in aqueous media initiated by trivalent manganese ion in the presence of thiourea shows characteristic features of heterogeneous polymerization. The reaction mixture, though homogeneous before the initiation of polymerization, becomes heterogeneous as soon as the polymerization starts, due to the insolubility of polyacrylonitrile (PAN) in the aqueous phase.

From the proportionalities obtained between the measurable parameters and variables, a reaction scheme has been suggested, involving initiation by organic free radical produced by the interaction of Mn(III) with thiourea and termination by mutual combination of polymer chains.

$$Mn^{3+} + TU \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Complex (TU = thiourea)} \qquad (1)$$

$$\text{Complex} \xrightarrow{k_r} R^{\cdot} + Mn^{2+} + H^+ \qquad (2)$$

$$R^{\cdot} + Mn^{3+} \xrightarrow{k_0} \text{Oxidation products} + Mn^{2+} \qquad (3)$$

Initiation:

$$R^{\cdot} + M \xrightarrow{k_i} RM_1^{\cdot} \qquad (4)$$

Propagation:

$$\mathrm{R\text{-}M_1^{\bullet}} + \mathrm{M} \xrightarrow{k_p} \mathrm{R\text{-}M_2^{\bullet}}$$

$$\vdots$$

$$\mathrm{RM_{n-1}^{\bullet}} + \mathrm{M} \xrightarrow{k_p} \mathrm{R\text{-}M_n^{\bullet}} \tag{5}$$

$$\mathrm{R\text{-}M_n^{\bullet}} + \mathrm{R\text{-}M_m^{\bullet}} \xrightarrow{k_t} \text{Polymer} \tag{6}$$

On applying the steady-state principle to the primary radical $R^{\bullet}$ as well as to the growing radical $R\text{-}M_n^{\bullet}$ and making the usual assumption that the radical activity is independent of the radical size, we obtain the rate expression (7).

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

The second term in Eq. (7) is due to reaction (3).
If $k_0 [\mathrm{Mn}^{3+}] \gg k_i [\mathrm{M}]$, this expression reduces to Eq. (8):

$$-d[\mathrm{Mn}^{3+}]/dt = 2 k_r K_1 [\mathrm{Mn}^{3+}]_{eq} [\mathrm{TU}] \tag{8}$$

Since the measured rates $-d[\mathrm{Mn}^{3+}]/dt$ apply to total $[\mathrm{Mn}^{3+}]$ regardless of the species and since

$$[\mathrm{Mn}^{3+}]_T = [\mathrm{Mn}^{3+}]_{eq} (1 + K_1 [\mathrm{TU}])$$

we obtain Eq. (9):

$$-d[\mathrm{Mn}^{3+}]/dt = 2k_r K_1 [\mathrm{Mn}^{3+}] [\mathrm{TU}]/(1 + K_1 [\mathrm{TU}]) \tag{9}$$

The polymerization rates for $k_p [\mathrm{RM}^{\bullet}] \gg k_i [\mathrm{R}^{\bullet}]$ are given by Eq. (10):

$$\frac{-d[\mathrm{M}]}{dt} = \frac{k_p k_i^{1/2} (k_r K_1 [\mathrm{Mn}^{3+}]_{eq} [\mathrm{TU}])^{1/2} [\overline{\mathrm{M}}]^{3/2}}{k_t^{1/2} (k_0 [\mathrm{Mn}^{3+}] + k_i [\mathrm{M}])^{1/2}} \tag{10}$$

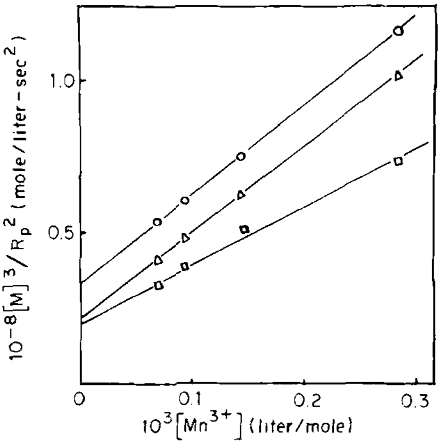

FIG. 4. Plots of $(1/R_p^2)\,[M]^{3+}$ vs. $[Mn^{3+}]^{-1}$: (○) 30°C; (△) 35°C; (□) 40°C. $[\bar{H}^+] = 1.1$ M, $\mu = 1.2$ M, [AN] = 0.754 M, [TU] = 1×10^{-3} M.

TABLE 1. Values of Rate Parameters for the Polymerization of Acrylonitrile (AN) Initiated by the Mn^{3+}-Thiourea Redox System

Temp (°C)	$10^{-2} \times k_p/k_t^{1/2}$ (liter-sec/mole)$^{1/2}$	$k_0/k_i \times 10^{-2}$
30	4.82	6.26
40	9.12	8.40

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

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

Now Eq. (10) can be rearranged to

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

The plots of $(-d[M]/dt^{-2}$ versus $[TU]^{-1}$ are linear with intercept on the ordinate (Fig. 3). From the intercepts of these plots we can calculate the ratio $k_p/k_t^{1/2}$. Equation (12) also requires that the plots of $(-d[M]/dt)^{-2}$ $[M]^3$ versus $[Mn^{3+}]^{-1}$ are linear with intercept $k_t(k_0/k_p^{2})k_ik_rK_1$ [TU] (Fig. 4). Using the values of $k_p/k_t^{1/2}$, the ratio k_0/k_i can be calculated (Table 1) from these intercepts.

ACKNOWLEDGMENT

The authors acknowledge their gratefulness to UGC, India for offering a Junior research fellowship to one of them (MCN).

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Accepted by editor March 6, 1978
Received for publication April 14, 1978