

Aqueous Polymerization of Acrylonitrile by Persulphate Disulphite Redox System Catalysed by Mn^{2+} Ion: A Kinetic Study

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Abstract: Polymerization of the acrylonitrile monomer (M), initiated by a persulphate - Mn^{2+} - disulphite redox system was investigated kinetically, over a temperature range of 25-45°C in aqueous medium under oxygen atmosphere. The incorporation of metal ion, Mn^{2+} , with persulphate - disulphite redox system and rate of polymerization (R_p) has been studied at various concentrations of monomer and initiator. The polymerization exhibited a strong dependence on the concentration of Mn^{2+} . That is, at low concentration of Mn^{2+} , $R_p \propto [M] [S_2O_8^{2-}]^{1/2} [HSO_3^-]^{1/2}$ while at high Mn^{2+} concentration, $R_p \propto [M] [S_2O_8^{2-}]^{1/2} [Mn^{2+}]^{1/2}$. The degree of polymerization is found to increase with increase in concentration of monomer and decrease in concentration of persulphate, manganese, and disulphite. The influence of organic solvents and temperature on the rate of polymerization has also been investigated and energy of activation was calculated to be 30.6 k J/mol. On the basis of experimental results, a suitable scheme has been proposed and a rate expression has been derived.

Keywords: Polymerization, acrylonitrile, persulphate, disulphite, manganese, monomer, kinetics, oxygen atmosphere, temperature

1. Introduction

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation states in aqueous medium can provide valuable information regarding mechanistic details of the elementary steps¹⁻⁸. A review of manganese (II) reactions shows that these reactions proceed via free radical mechanisms which are capable of initiating radical polymerization⁹⁻¹². Thus manganese (II) in the presence of various inorganic and organic reducing agents has been used as an effective initiator for the polymerization of vinyl monomers. The decomposition of persulphate and its activation by reductants and metal ions have been studied earlier¹³⁻¹⁵. In the present study the polymerization of acrylonitrile has been carried out by a three-component system consisting of persulphate- Mn^{2+} - disulphite in aqueous medium under atmospheric oxygen¹⁶. The monomer chosen for the study is acrylonitrile since its polymers have major industrial applications.

2. Experimental

The monomer acrylonitrile was purified by distilling at low pressure under nitrogen atmosphere, after washing with 5% NaOH, 3% H_3PO_4 and water. The middle fraction was collected and stored at 5°C. Potassium persulphate (s.d. fine - 99 %) and sodium disulphite (CDH - 99.7%) are used without any purification and their fresh solutions are used for each trial. $MnSO_4$ was used as received and its aqueous solution was prepared. Doubly distilled water was used throughout the experiment. The polymerization reaction was carried out in the presence of atmospheric oxygen in pyrex glass vessels. In a typical experiment, a mixture of known amounts of monomer, Mn^{2+} , disulphite and water (to keep the total volume constant) was thermally equilibrated at the desired temperature and then oxidant, $K_2S_2O_8$ was added. After specific time intervals

adding ice cold water and dilution, arrested the reaction. The percentage conversions versus time plots were drawn after eliminating the induction period. The rate of polymerization was determined gravimetrically. The rate of persulphate disappearance was determined by the method of Kolthoff and Carr¹⁷.

For determining the viscosity average molecular weight (M_v) of the resulting polymer, viscosity measurements were carried out with an Ostwald's viscometer and the M_v value was evaluated by using the Mark - Houwink equation given by Stockmayer and Cleland¹⁸ $[\eta] = 3.235 \times 10^{-4} M_v^{0.72}$ at 30° C for polyacrylonitrile in dimethylformamide (DMF).

3. Result and Discussion

Effect of [Persulphate]

When the concentration of persulphate is raised in the range 0.5 to $2.0 \times 10^{-2} \text{ mol dm}^{-3}$, at the concentration of Mn^{2+} (1.5 to $3.0 \times 10^{-3} \text{ mol dm}^{-3}$), the rate of polymerisation (R_p) are found to increase due to the increase in the concentration of the active species²⁰. The exponent of $[K_2S_2O_8]$ is found to be 0.5 from a plot of $\log R_p \ll \log [K_2S_2O_8]$ (Figure 1). This clearly indicates that the termination occurs through bimolecular interaction of growing polymer chain radicals. Increasing the [Persulphate] beyond the above said concentration provides more chance for premature termination of growing chain radicals which reduces the degree of polymerization and molecular weight.

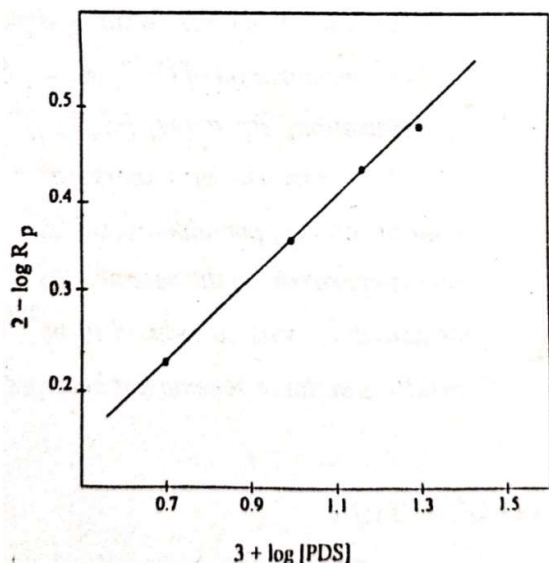


Figure 1: Plot of $\log R_p$ versus $\log [PDS]$. $[PDS] = 0.005, 0.01, 0.015$ and 0.02 mol dm^{-3} , $[Mn^{2+}] = 0.002 \text{ mol dm}^{-3}$, $[HSO_3^-] = 0.001 \text{ mol dm}^{-3}$, $[M] = 0.6068 \text{ mol dm}^{-3}$ at 26°C .

Effect of $[Mn^{2+}]$:

The dependence of rate of polymerization on redox components varies with Mn^{2+} concentration in the system. At lower concentration ($1.5 \times 10^{-3} \text{ mol/dm}^3$) the rate varies with the half power of the [persulphate] and [disulphate] while at the higher value ($3.0 \times 10^{-3} \text{ mol/dm}^3$) the rate varies with the half power of [persulphate] and $[Mn^{2+}]$ (Fig 2). In both the cases an order of unity with respect to monomer is constant.

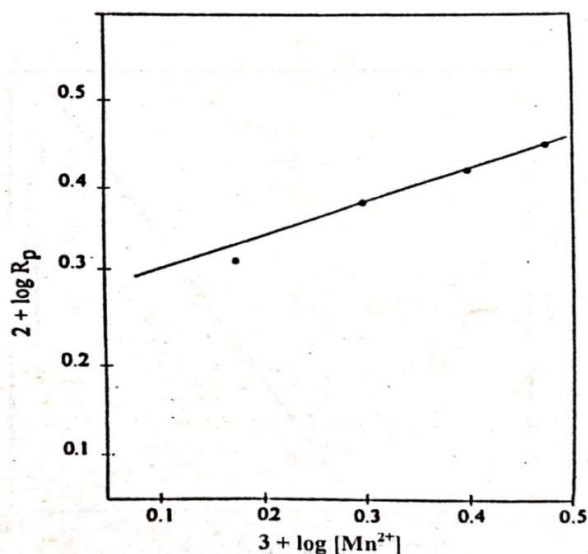


Figure 2: Plot of $\log R_p$ versus $\log [Mn^{2+}]$. $[Mn^{2+}] = 0.0015, 0.002, 0.0025, 0.003 \text{ mol dm}^{-3}$, $[HSO_3^-] = 0.001 \text{ mol dm}^{-3}$, $[M] = 0.6068 \text{ mol dm}^{-3}$, $[PDS] = 0.01 \text{ mol dm}^{-3}$ at 26°C .

The decrease in the viscosity $[\eta]$, $[M]$ and the degree of polymerization $[P_n]$ is observed with increased Mn^{2+} concentration which further supports the possibility of

bimolecular termination by mutual combination of growing polymer chain radicals.

Effect of [Disulphite]:

The effect of [disulphite] on the rate of polymerization has been studied by varying its concentration in the range 0.7 to $2.0 \times 10^{-3} \text{ mol/dm}^3$ (Figure 3). The results clearly indicate that the effect of disulphite on the polymerization kinetics is dependent on $[Mn^{2+}]$. At lower $[Mn^{2+}]$ ($1.5 \times 10^{-3} \text{ mol/dm}^3$) a half order dependence is exhibited by disulphite while at higher $[Mn^{2+}]$ ($3.0 \times 10^{-3} \text{ mol/dm}^3$) a zero-order dependence of rate of polymerization on disulphite is observed.

The results may be discussed as follows. (i) At lower $[Mn^{2+}]$ an increase in the initial rate and percentage conversion is observed with increase in [disulphite]. This observation is quite obvious as on increasing [disulphite] greater number of primary free radicals will be generated [Eq.2 and 3] and therefore the initial rate of polymerization increases. (ii) When [disulphite] is increased at higher $[Mn^{2+}]$ then almost no change in the initial rate of polymerization and percentage conversion is observed which indicates a zero-order dependence of the rate on [disulphite]. The results may be explained by the fact that at higher $[Mn^{2+}]$ the following two reactions become significant viz. (a) With the increase in [disulphite] the production of primary free radicals increase and (b) the termination of growing chains by Mn^{2+} increases. It may lead to a zero-order dependence of polymer rate on [disulphite]. It is clearly shown by data (Table 1) that increase in [disulphite] the molecular weight decreases, which support the idea of pre dominating termination step.

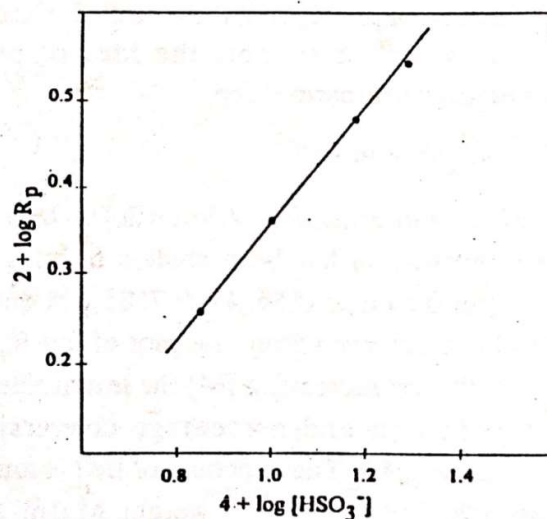


Figure 3: Plot of $\log R_p$ versus $\log [HSO_3^-]$. $[HSO_3^-] = 0.0007, 0.001, 0.0015, 0.002 \text{ mol dm}^{-3}$, $[M] = 0.6068 \text{ mol dm}^{-3}$, $[PDS] = 0.01 \text{ mol dm}^{-3}$, $[Mn^{2+}] = 0.002 \text{ mol dm}^{-3}$ at 26°C .

Effect of [Monomer]:

The effect of increasing [acrylonitrile] on the rate of polymerization has been studied by varying the [M] in the range 0.3034 -0.7585 mol/dm³.

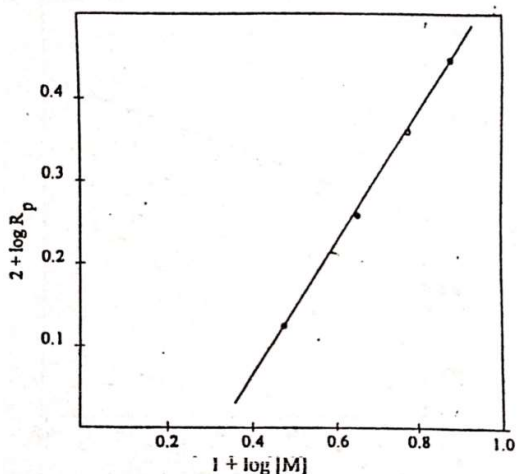


Figure 4: Plot of $\log R_p$ versus $\log [M]$. $[M] = 0.3034, 0.4551, 0.6068, 0.7585 \text{ mol dm}^{-3}$, $[PDS] = 0.01 \text{ mol dm}^{-3}$, $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}] = 0.002 \text{ mol dm}^{-3}$ at 26°C .

It has been observed from the plot of $\log R_p > \log [M]$ that on increasing [M] the initial rate of polymerization and percentage conversion increases (Figure 4.). The exponent of [M] is found to be one. The molecular weight M_v of the polymer also increases with monomer concentration.

Effect of Temperature

The effect of varying the temperature of polymerization medium has been studied in the range of $25-45^\circ\text{C}$. It is observed that with the increase in temperature both the initial rate and percentage conversion increase due to the

increase in the formation of free radicals (Figure 5). The energy of activation has been calculated with the help of Arrhenius plot to be 30.6 kJ mol^{-1} .

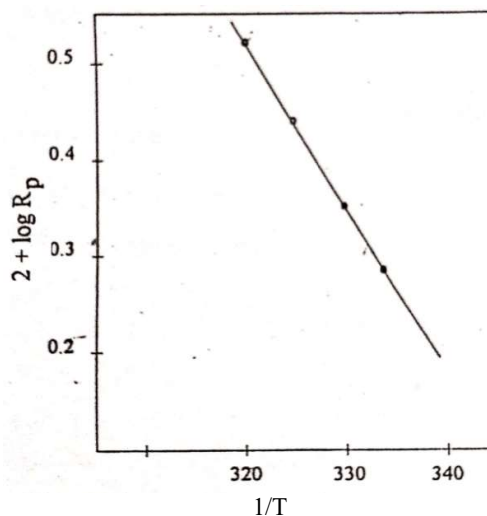


Figure 5: Arrhenius plot of $\log R_p$ versus $1/T$. $[PDS] = 0.01 \text{ mol dm}^{-3}$, $[\text{HSO}_3^-] = 0.001 \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}] = 0.002 \text{ mol dm}^{-3}$, $[M] = 0.6068 \text{ mol dm}^{-3}$, Temperature = $26^\circ\text{C}, 30^\circ\text{C}, 35^\circ\text{C}, 40^\circ\text{C}$.

Effect of Organic Solvents:

Addition of water miscible organic solvents [5% v/v] such as MeOH, EtOH and DMF to the reaction medium increases the rate of polymerization. The observed increase in rate and maximum conversion is due to the increased number of free radicals produced by the interaction of oppositely charged species, thus involving a negative dielectric effect. The addition of these organic solvents lowers the dielectric constant of the reaction medium and facilitates the production of large number of free radicals^{14,20}.

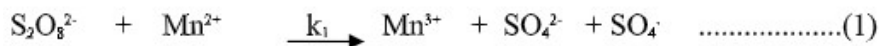
Table 1: Effect of Concentration of Persulphate (PDS), Metadisulphite (MDS), Acrylonitrile (AN) and Manganese (II) on the rate of Polymerization (R_p) and Molecular Weight (M_v) of Polyacrylonitrile

$[PDS]10^3$ mol dm^{-3}	$[MDS]10^3$ mol dm^{-3}	$[AN]$ mol dm^{-3}	$\text{Mn (II)}10^3$ mol dm^{-3}	$R_p \times 10^2$ $\text{mol dm}^{-3} \text{ s}^{-1}$	Mol.Wt. M_v
0.5	1.0	0.6068	2.0	1.70	91040
1.0	1.0	0.6068	2.0	2.30	84080
1.5	1.0	0.6068	2.0	2.72	71180
2.0	1.0	0.6068	2.0	3.12	60040
1.0	0.5	0.6068	2.0	1.80	90240
1.0	1.0	0.6068	2.0	3.05	84080
1.0	1.5	0.6068	2.0	3.40	71130
1.0	2.0	0.6068	2.0	1.70	64044
1.0	1.0	0.3034	2.0	1.33	74076
1.0	1.0	0.4551	2.0	1.83	81068
1.0	1.0	0.6068	2.0	1.32	84080
1.0	1.0	0.7585	2.0	2.76	96340
1.0	1.0	0.6068	1.5	2.06	90050
1.0	1.0	0.6068	2.0	2.32	84080
1.0	1.0	0.6068	2.5	2.50	67272
1.0	1.0	0.6068	3.0	2.84	51248

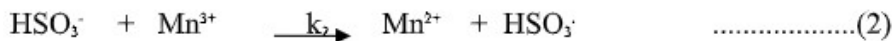
Mechanism and Rate Law

A stepwise possible mechanism for the polymerization of acrylonitrile by the persulphate-Mn²⁺-disulphite redox system may be outlined as follows.

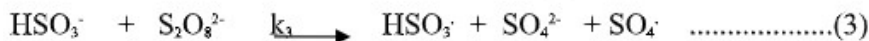
(a) Formation of the free radicals:



(R)



(R)



(R)

(R)

(b) Initiation:



(c) Propagation:



(d) Termination:



Applying the steady state principles to all free radicals, a rate equation can be derived as follows.

$$d[\text{R}\cdot]/dt = k_1[\text{S}_2\text{O}_8^{2-}][\text{Mn}^{2+}] + k_2[\text{HSO}_3\cdot][\text{Mn}^{3+}] + k_3[\text{HSO}_3\cdot][\text{S}_2\text{O}_8^{2-}] - k_i[\text{R}\cdot][\text{M}] = 0 \quad \dots\dots\dots (7)$$

$$d[\text{Mn}^{3+}]/dt = k_1[\text{S}_2\text{O}_8^{2-}][\text{Mn}^{2+}] - k_2[\text{HSO}_3\cdot][\text{Mn}^{3+}] = 0$$

$$[\text{Mn}^{3+}] = k_1[\text{S}_2\text{O}_8^{2-}][\text{Mn}^{2+}] / k_2[\text{HSO}_3\cdot] \quad \dots\dots\dots (8)$$

Substituting equation (8) in equation (7) we get,

$$\text{R}\cdot = 2k_1[\text{S}_2\text{O}_8^{2-}][\text{Mn}^{2+}] + k_3[\text{HSO}_3\cdot][\text{S}_2\text{O}_8^{2-}] / k_i[\text{M}] \quad \dots\dots\dots (9)$$

Under steady state conditions, the rate of initiation = rate of termination.>

$$k_i[\text{R}\cdot][\text{M}] = k_t[\text{RM}_n\cdot]^2 \quad \dots\dots\dots (10)$$

$$[\text{RM}_n\cdot] = (k_i)^{1/2}[\text{R}\cdot]^{1/2}[\text{M}]^{1/2} / (k_t)^{1/2} \quad \dots\dots\dots (11)$$

The rate of polymerisation is given by the rate of propagation,

$$R_p = k_p[\text{RM}_n\cdot][\text{M}] \quad \dots\dots\dots (12)$$

On substituting equation (9) in equation (11) and then in equation (12) we get,

$$R_p = k_p / (k_i)^{1/2} [\text{M}] [\text{S}_2\text{O}_8^{2-}]^{1/2} \{2k_1[\text{Mn}^{2+}] + k_3[\text{HSO}_3\cdot]\}^{1/2} \dots\dots (13)$$

Now let us analyze equation (13) with [Mn²⁺]

(i) Where $[Mn^{2+}]$ is of lower range, then we can assume that

$$\{k_3[HSO_3^-]\}^{1/2} \gg 2k_1[Mn^{2+}]^{1/2}$$

Now equation (13) is reduced to

$$R_p = k_p k_3 / (k_t)^{1/2} [M] [S_2O_8^{2-}]^{1/2} [HSO_3^-]^{1/2}$$

OR

$$R_p \propto [M] [S_2O_8^{2-}]^{1/2} [HSO_3^-]^{1/2} \dots\dots\dots (14)$$

(ii) At higher $[Mn^{2+}]$ we can assume that

$$\{2k_1[Mn^{2+}]\}^{1/2} \gg \{k_3[HSO_3^-]\}^{1/2}$$

Then equation (13) becomes

$$R_p = (2k_1)^{1/2} / (k_t)^{1/2} k_p [M] [S_2O_8^{2-}]^{1/2} [Mn^{2+}]^{1/2}$$

$$R_p \propto [M] [S_2O_8^{2-}]^{1/2} [Mn^{2+}]^{1/2} \dots\dots\dots (15)$$

The derived rate expression is in full agreement with experimental results.

4. Conclusion

The polymerization of vinyl monomers by the redox system is catalysed by manganese ion. The manganese (III) produced in situ reacts with the reductant producing free radicals capable of initiating vinyl polymerization. Further the reaction is catalysed by organic solvents due to negative dielectric constant effect. The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence for the existence of transient radical intermediates formed in situ. This allows the identification of the radicals as end groups of the polymer.

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