Chapter – 6
This chapter reveals that the redox polymerization of acrylonitrile initiated by the free radical generated by the potassium persulphate–ascorbic acid redox system has been investigated in an aqueous sulfuric acid medium in the temperature range 40–70°C. The rate of polymerization (Rp) and rate of potassium persulphate disappearance have been measured. A kinetic scheme has been proposed involving production of initiating radicals from oxidation of ascorbic acid by potassium persulphate ions and termination exclusively by the interaction of the chain radicals with persulphate ions. The scheme is consistent with experimental findings. The effect of some-water-miscible organic solvents and surfactants on the rate of polymerization was investigated. The temperature dependence of the rate was studied.

6.1.1 Introduction

Various redox systems have been used successfully for the polymerization of organic monomers in aqueous media \(^1\)–\(^{10}\). The redox polymerization has the advantage of very short induction period, relatively low energy of activation, production of high-molecular-weight polymers with high yields, easy control of the polymerization reaction at low temperature due to reduction of side reactions and the direct experimental proof of the transient radical intermediates \(^{11}\)–\(^{14}\). Commonly used oxidants include peroxides, persulphates, permanganates, etc and the salts of the transition metals. These
oxidants form potential redox systems with various reducing agents like alcohols, aldehydes, amines, amides, ketones, acids, thiols, etc. for the aqueous polymerization of vinyl monomers\textsuperscript{15-20}. However, redox initiation in organic solvents is not so much successful. Peroxide / tertiary amine\textsuperscript{21} or hydroperoxide-cobalt octate\textsuperscript{22} systems reported are not applicable for all vinyl polymerization. In fact redox reactions are more complicated than we thought, and presumably water involves in some steps of the reactions. In the present investigation, kinetics of polymerization of acrylonitrile initiated by potassium persulphate- ascorbic acid redox system in sulfuric acid medium has been studied.

6.1.2 Chemistry of Ascorbic acid (Vitamin-C)

Ascorbic acid is an organic acid with antioxidant properties. It is appearance is white to light yellow crystals or powder. It is water-soluble and slightly soluble in alcohol, insoluble in chloroform, benzene, petroleum ether, oils and fats. It is must be present in the diet of man to prevent scurvy. It cures scurvy and increase resistance to infection. Ascorbic acid acts as oxidation – reduction catalyst in the cell. It is readily oxidized, citrus juices should not be exposed to air for more than few minutes, before use. It is non-toxic and used as nutrition color fixing, flavoring and preservative in meats and other foods. The L- ascorbic acid is commonly known as vitamin C. It is used as reducing agent in analytical chemistry. It has molecular weight of 176.13 g/mol, density 1.65 and melting point 190\textsuperscript{0}C. The name “Ascorbic” comes from its property of preventing and curing of scurvy\textsuperscript{23}. 

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EXPERIMENTAL

6.2.3 Materials and methods

Acrylonitrile (S.D. Fine Chem. Mumbai India) was purified by the method of Bamford et al. The inhibitor free sample was washed thrice with deionized water to remove the trace of alkali water used for the preparations of solutions was obtained by double distilled water over alkaline permanganate and was deionized by passing through Biodeminrolit resin (Permutit Co., UK). All other chemicals such as potassium persulphate, sulphuric acid, ascorbic acid, methanol, ethanol, DMF, Cetyl trimethylammonium bromide, and triton x-100 were of analytical grade. A solution of potassium persulphate was prepared by triple distilled water and standardized with standard sodium thiosulphate solution using starch as an indicator. Triple distilled water was used throughout the experiment, pure nitrogen obtained by passing through a column of Fieser’s solution and distilled water was used for the deaeration condition of all experimental systems.

6.1.4 Kinetic Measurements

Inhibitor-free acrylonitrile (0.607M) monomer, ascorbic acid (1.0 X 10^{-2} mol / dm^{3}) and water (to keep the total volume constant) were taken in reaction vessels and thermostated at 50° C. the system was flushed with oxygen-free nitrogen for about 20-30 min to expel the dissolved oxygen. At the end of the duration, potassium persulphate solution (4.0 X 10^{-3} mol / dm^{3}) was added to the reaction vessels and shaken well. The reaction vessel was then sealed with rubber gasket to ensure inert atmosphere. The polymerization starts without any induction period. After about 60 min the reaction was arrested by adding a known amount of ferrous solution or by cooling the reaction mixture to 0° C. The polyacrylonitrile was filtered from the reaction mixture using funnels,
washed several times with distilled H$_2$O and dried at 70°C to a constant weight. Finally the rate of polymerization (Rp) and potassium persulphate disappearance (-R$_m$) were determined$^{73}$ gravimetrically.

### 6.1.5 Molecular Weight Determination

The molecular weight M$_v$ of the purified sample of polyacrylonitrile product was determined by viscometry method. A 1% solution of the polymer in DMF was filtered through fitted glass filter and placed in an Ubbelhode type suspended level dilution viscometer. The intrinsic viscosity $\eta$ for the reaction mixture was determined and M$_v$ values were calculated using the following Mark-Houvink equation given by Stockmayer and Cleland$^{74}$. $\eta = (3.335 \times 10^{-4}) \times M_v^{0.72}$ at 30°C for polyacrylonitrile in DMF. The molecular weight of the polymer product under standard conditions was found to be 6.75x10$^4$. It increases with monomer concentration and decreases with increase in [potassium persulphate], [ascorbic acid] or temperature. This effect is attributed to the fact that increases in [potassium persulphate], [ascorbic acid] or temperature provides more chances for premature termination of growing chain polymer radicals, thus reducing the degree of polymerization. Behari et al$^{75}$, have reported similar effects. density and R.I determined using the density bottle and refractometer (1.256 & 1.353) respectively.

### 6.1.6 Results and Discussion

Under the conditions of high temperature (40°C) it was found that there was no polymerization of the monomer even after 75 min with potassium persulphate alone was used as an initiator. But with potassium persulphate-ascorbic acid as redox initiator, it was noticed that the polymerization reaction proceeded without any induction period. The steady state was attained within 75 min. The polymerization of acrylonitrile initiated by potassium persulphate-ascorbic acid redox system takes place at a measurable rate in the temperature
range 50-70°C. The rate of potassium persulphate disappearance (-R_m) was found to be independent for potassium persulphate at standard concentration. A plot of (R_m) versus [potassium persulphate] was linear and passed through the origin. A plot of 1/Rm versus 1/ [ascorbic acid] was linear with an intercept on the rate axis, indicating Line weaver-Burk kinetics for complex formation.\(^77\)

### 6.1.7 Rate of polymerization

The rate of polymerization (Rp) increases with the increase of monomer concentration (0.151-1.518M). A plot of log Rp versus log [M] was a straight line with a slope equal to one or unity. (Fig.1), and a plot of Rp versus [M] was a straight line with zero intercept indicating that the order with respect to monomer was unity. Rp increases linearly with increase in the ascorbic acid concentration up to [1.0 – 5.0 x 10-2 M]. A plot of log Rp versus log [ascorbic acid] was a straight line passing through the origin (Fig 2). This showed that the order with respect to [ascorbic acid] is 0.11. A regular increase in Rp was also noticed with the increase in [potassium persulphate] [4.0-20.0. x 10 –3 M]. A plot of log Rp versus log [potassium persulphate] was linear, having a slope of 1.11 with zero intercept (Fig 3), indicating that the order with respect to [potassium persulphate] is unity. These observations suggest that the termination of polymerization may be caused by the mutual combination of growing polymer radicals 76.

The rate of potassium persulphate disappearance (-R_m) was first order with respect to potassium persulphate and is independent of acrylonitrile concentration. It depends on [potassium persulphate] and [ascorbic acid]. A plot of -1/ R_m versus 1/[ascorbic acid] is Line weaver-Burk kinetics for complex formation 77. (Table 1 and Fig 5).
6.1.8 Reaction mechanism and rate law

The polymerization of acrylonitrile (AN) in aqueous medium initiated by potassium persulphate-ascorbic acid redox system, shows characteristic features of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts because of the insolubility of the polymer (PAN) in the aqueous media. From the kinetic results, a reaction has been proposed involving the imitation by organic free radicals generated by the interaction by the potassium persulphate with COOH.

6.1.9. Mechanism

\[
\begin{align*}
\text{HO} & \quad \text{C} \quad \text{C} \quad \text{OH} \\
\text{O} & \quad \text{C} \quad \text{CHCH(OH)CH}_2\text{OH} \\
\text{O_2} & \text{slow} \quad \text{O}_2 \\
\text{O} & \quad \text{C} \quad \text{C} \quad \text{O}^* \\
\text{O} & \quad \text{C} \quad \text{CHCH(OH)CH}_2\text{OH} \\
\text{OH} & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{O}^* \\
\text{O} & \quad \text{C} \quad \text{CHCH(OH)CH}_2\text{OH} \\
\text{OH} & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{O}^* \\
\text{O} & \quad \text{C} \quad \text{CHCH(OH)CH}_2\text{OH} \\
\end{align*}
\]

OR

Potassium persulfate - ascorbic acid

\[
\begin{align*}
\text{S}_2\text{O}_8^{2-} & \longrightarrow 2\text{SO}_4^{-} \\
\text{SO}_4^{-} + \text{H}_2\text{O} & \longrightarrow \text{SO}_4^{2-} + \text{O}^*\text{H} + \text{H}^+ \ldots \ldots \ldots (2) \\
\text{O}^*\text{H} + \text{AH}^- & \longrightarrow \text{AH}^* + \text{OH}^- \\
\text{AH}^* + \text{S}_2\text{O}_8^{2-} & \longrightarrow \text{A} + \text{SO}_4^{2-} + \text{SO}_4^{-} + \text{H}^+
\end{align*}
\]
Mishra and Gupta reported the formation of a complex b/w monomers and peroxydisulfate which later dissociates to liberate initiating primary radicals.

Roskin proposed that the hydroxyl radical formed in the system can also takes part in the initiation.

\[
AA + S_2O_8^{2-} \quad \xrightarrow{k} \quad \text{Complex}
\]

\[
\text{Complex} \quad \xrightarrow{} \quad R^* + H^+ + 2SO_4^-
\]

**Initiation**

\[
k_i
\]

\[
M + R^* \quad \xrightarrow{} \quad RM^*
\]

**Propagation**

\[
k_p
\]

\[
RM^* + M \quad \xrightarrow{} \quad RM M^*
\]

\[
\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots
Applying steady state approximation

- \( d / dt [R\cdot] = kd[\text{complex}] - kt[M][R\cdot] = 0 \)

\( k = [\text{complex}] / [AS] [PS \ (II)] \)

\( [\text{complex}] = k [AS] [PS \ (II)] \)

\( kd k[AS] [PS \ (II)] – ki [M] [R\cdot] = 0 \)

\( [R\cdot] = kd k [PS \ (II)] [AS] / ki [M] \)

\( ki [R\cdot] [M] = -kt [RM\cdot n] [RM\cdot n] = kt [RM\cdot n]^2 \)

\( [RM\cdot n]^2 = (ki / kt) [R\cdot][M] \)

\( [RM\cdot n] = (ki / kt)^{1/2} [R\cdot]^{1/2} [M]^{1/2} \)

\( kp = [RM\cdot n][M] \)

\( Rp = kp (ki / kt)^{1/2} [R\cdot]^{1/2} [M]^{1/2} \)

\( Rp = kp (ki / kt)^{1/2} kp (kd k / kt)^{1/2} [[PS \ (II)] [AS] / [M] \}^{1/2} [M]^{3/2} \)

\( Rp = kp (kd k / kt)^{1/2} [PS \ (II)]^{1/2} [AS]^{1/2} [M]^{1/2} \)

\( Rp = kp (kd k / kt)^{1/2} [PS \ (II)]^{1/2} [AS]^{1/2} \)

Thus the dependence of \( Rp \) on \([M] \cdot [PS \ (II)]\) and \([AS]\) all of which are observed, are consistent with the experimental results. The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence of the existence of transient radical intermediates generated in redox reactions. It also enables the identification of these radicals as end groups of the polymer. Further work on the kinetics of polymerization, various vinyl monomers initiated by the reaction of PS (II) and other transition metals ions, with suitable reductants is in progress in our laboratory.

6.1.10 Rate dependence on monomer concentration

The rate of polymerization increases with increasing monomer concentration. The availability of monomer molecules in the propagation step increases, which obviously increases the rate of polymerization. The order of the reaction with respect of monomer concentration is calculated from the plot
of log Rp versus log [M] (Fig 1). The order with respect to acrylonitrile concentration is found to be unity in the range of 0.1518-1.5188 mol / dm$^3$. At higher [AN] the rate decreases, because of increase of in viscosity of the medium due to the solubility of the polymer in the monomer, rendering the diffusion of the ions difficult through the medium. An order of a reaction is higher than unity is indicative of the occurrence of cage effect$^{78}$.

6.1.1 Rate dependence on [potassium persulphate]

Rate of polymerization increases with increase in the concentration of potassium persulphate it is due to increases in the concentration of active species. The order of the reaction with respect to potassium persulphate is found to be unity in the concentration range 4.0 X 10$^{-3}$- 20.0 X 10$^{-3}$ mol / dm$^3$. This is also clearly indicates that the termination occurs through unimolecular interaction of growing polymer chain radical. The molecular weight (Mv) of polyacrylonitrile decreases with increases in [potassium persulphate]. This can be explained by the fact that increasing the concentration of [potassium persulphate] provides more chances for premature termination growing chain radicals, which reduce the degree of polymerization$^{79}$. Fig.2

6.1.2 Rate dependence on Ascorbic acid concentration

The increase of ascorbic acid concentration, increase the Rp and reaches optimum level and then it is decreasing gradually. The exponent (slope) of the ascorbic acid was found to be fractional order (0.11) from the plot of log Rp versus log [ascorbic acid] in the concentration range of 1.0 X 10$^{-2}$– 5.0 x 10$^{-2}$ mol / dm$^3$ (Fig.3). At higher concentration of ascorbic acid the rate decreases due to the chain transfer or mutual interaction of the growing polymer chain radicals.
6.1.13 Rate dependence on H$_2$SO$_4$ concentration

The kinetic measurements were performed in H$_2$SO$_4$ aqueous solution of different ion concentration. The rate of polymerization (Rp) decreases with an increase in [H$^+$] ion, indicates that the hydrolyzed species of potassium persulphate is more reactive than the unhydrolysed species and also that the unprotonated form of ascorbic acid is more reactive than the protonated form. The order with respect to H$^+$ ion concentration was found to be inverse fractional order (-0.5) from the plots of log Rp versus log [H$^+$] (Fig 4).

6.1.14 Rate dependence on Temperature

When temperature of reaction mixture is increased from 40-70$^\circ$C, the initial rate of polymerization (Rp) and % conversion was increases and beyond 70$^\circ$C fall in the initial rate & limiting conversion is observed. The observed value increases are due to fact that, with increase in temperature, the rate of active center formation increases, which consequently increases the initial rate and conversion with temperature. Further beyond 70$^\circ$C, which may cause an increase in the rate of primary radical termination, thus decreasing the initial rate and limiting conversion? The overall energy of activation (Ea) has been calculated from the Arrhenius plot of log Rp versus 1/T, (Fig 5) in the temperature range of 40-70$^\circ$C. Activation energy (Ea) = 11.49 kJ / mol. The other activation parameters calculated from the Eyring plot are as follows: \( \Delta H^\ne = 45.40 \text{ kJ / mole} \), \( \Delta S^\ne = -166.87 \text{ JK}^{-1}/\text{mole} \), and \( \Delta G^\ne = 72.89 \text{ kJ / mole} \).

6.1.15 Rate dependence on organic Solvents

Since the properties of a polymer mostly depend on the nature of the medium, various water–miscible organic solvents such as methanol, DMF and ethanol1 have been observed their effect on the rate of polymerization (Rp). When added to the reaction mixture in equal volume (5%v/v) a depression in
the initial rate of polymerization and the limiting conversion has been observed. The increasing order of depression by these solvents is methanol < ethanol < DMF.

The cause of depression in the rate of polymerization and % conversion by the added organic solvents may be explained.

1) When the organic solvents are added to the reaction mixture, they cause a decrease in the area of shielding of a strong hydration layer in aqueous medium, which results in the termination of radical end of the growing chain.

2) Some amount of catalyst may be consumed in the oxidation of these organic solvents due to which the concentration of catalyst decreases and a depression in rate is observed. The sluggish radicals thus produced may not be equally capable of initiating the polymerization.

### 6.1.16 Rate dependence on surfactants

Addition of anionic surfactant, sodium lauryl sulfate (SLS) increases the Rp above and below the CMC value. The cationic surfactant cetyltrimethyl ammonium bromide (CTABr) is increasing the rate above and below CMC value. In contract, nonionic surfactants like triton x-100 have no effect on the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization.

### 6.1.17 Conclusion

Acrylonitrile is polymerized in a nitrogen atmosphere by the redox system of potassium persulphate / ascorbic acid via a free radical mechanism. The polymerization reaction with respect to monomer concentration is 1.0. And the reaction order related to the potassium persulphate and ascorbic acid
concentrations are 1.11 and 0.11 respectively, which indicates that bimolecular mechanism is suggested and the following rate equation is derived:

\[ Rp = k[M]^{1.0} \text{[potassium persulphate]}^{1.1} \text{[thiourea]}^{0.11} \]

From the Arrhenius plot, the overall energy of activation (Ea) has been calculated as 11.49 kJ / mol in the investigated range of temperatures.

**Table I**

**Plots of 1 / (-Rm) versus 1 / [As]**

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<tr>
<th>1 / [As]</th>
<th>1 / (-Rm)</th>
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<tr>
<td>1000</td>
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</tr>
<tr>
<td>500</td>
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Table: 2. Effect of variations of [PS (II)], [AS], [Monomer] and Temperature on the rate of polymerization

<table>
<thead>
<tr>
<th>[PS(II)] (10^2) (mol / dm³)</th>
<th>[AS] (10^2) (mol / dm³)</th>
<th>[AN] (mol / dm³)</th>
<th>[H₂SO₄] (10^4) (mol / dm³)</th>
<th>Temperature (K)</th>
<th>Rp (10^5) (S⁻¹)</th>
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Figure 1 Effect of [monomer] on the rate of polymerization, 
[PS(II)] = 4.0 x 10^{-3} mol / dm^3, [AS] = 1.0 x 10^{-2} mol / dm^3,
[Monomer] = (0.1518-1.5188) x 10^{-2} mol / dm^3 , Temperature = 323 K.
[ H_2SO_4 ] = 2.0 x 10^{-3} mol / dm^3
Figure. 2. Effect of [PS (II)] on the rate of polymerization,

[PS(II)] = 4.0-20.0 x 10^{-3} \text{ mol/dm}^3, \ [AS] = 1.0 \times 10^{-2} \text{ mol/dm}^3,

[Monomer] = 0.0675 \times 10^{-2} \text{ mol/dm}^3, \ [H_2SO_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3

Temperature = 323 \text{ K.}
Figure. 3. Effect of [ascorbic acid] on the rate of polymerization.

[PS(II)] = 4.0 x 10^{-3} \text{ mol / dm}^3, \ [AS] = 1.0-5.0 \times 10^{-2} \text{ mol / dm}^3

[Monomer] = 0.6075 \times 10^{-2} \text{ mol / dm}^3, \ [H_2SO_4] = 2.0 \times 10^{-3} \text{ mol / dm}^3

Temperature = 323 K
Figure 4 Effect of $\text{H}_2\text{SO}_4$ on the rate of polymerization,

$[\text{PS(II)}] = 4.0-20.0 \times 10^{-3}$ mol / dm$^3$, $[\text{AS}] = 1.0 \times 10^{-2}$ mol / dm$^3$,

$[\text{Monomer}] = 0.0675 \times 10^{-2}$ mol / dm$^3$, $[\text{H}_2\text{SO}_4] = 2.0 \times 10^{-3}$ mol / dm$^3$,

Temperature = 323 K.
Figure 5 Effect of temperature on the rate of polymerization, [PS(II)] = 4.0-20.0 x 10^{-3} mol / dm^3, [AS] = 1.0 x 10^{-2} mol / dm^3,
[Monomer] = 0.0675 x 10^{-2} mol / dm^3, Temperature = 313-353 K. [H_2SO_4] = 2.0 x10^{-3} mol / dm^3
Fig: 6. I R SPECRA OF POTASSIUM PERSULPHATE – ASCORBIC ACID ACRYLONITRILE REDOX SYSTEM
REFERENCES

63. V. A. Yakovlev, N. P. Pymarchuk and K. P.
64. L. P. Mazo, A. I. Ezrichev and E. S. Roskin. Zh- Prikl Khim (Leningard)
THE STUDY OF FREE RADICAL POLYMERIZATION OF ACRYLONITRILE BY OXIDATION-REDUCTION SYSTEM USING POTASSIUM PERSULPHATE-THIOUREA IN AQUEOUS MEDIUM

SECTION-B

This chapter deals with the study of polymerization kinetics of acrylonitrile with the K$_2$S$_2$O$_8$/Thiourea redox system has been investigated volumetrically in an aqueous medium in the temperature range of 40-80°C. The rate of polymerization (Rp) and rate of potassium persulphate disappearance have been measured. The effects of some-water-miscible organic solvents, cationic, anionic, non-ionic surfactants and complexing agents on the rate of polymerization were investigated. The temperature dependence of the rate was studied and the activation parameters were computed using the Arrhenius and Eyring plots. The effects of organic solvents on polymerization were also investigated. All of them depressed both the initial rate and limiting conversion. A mechanism consistent with the experimental data involving K$_2$S$_2$O$_8$-Thiourea complex formation, which generates free radicals, is suggested. Molecular weight of the polymer was determined by viscometry.
6.2.1 Introduction

Redox polymerization has the advantage of very short induction time, low activation energy (40-85 kJ/mol), production of high-molecular-weight polymers with high yields, easy control of the polymerization reaction at low temperature due to reduction of the side reactions and the direct experimental proof of the transient radical intermediates. In redox systems, oxidants form initially a complex by reacting with simple organic molecules, which then decompose unimolecularly to produce free radicals that initiate polymerization. Numerous redox pairs containing organic and inorganic compounds as polymerization initiator have been used successively. Commonly used oxidants include peroxides, persulphates, permanganates etc, and the salts of transition metals. These oxidants form potential redox systems with various reducing agents like alcohols, aldehydes, amines, amides, ketones, acids, thiols, etc., for the aqueous polymerization of vinyl monomers. Low-temperatures redox polymerization of vinyl monomers is of importance, especially for industrial viewpoints. Besides its economical benefits, suppression of side reactions such as branching is its additional advantage over common thermal initiation methods. In this way various redox systems have used successfully for the polymerization of organic vinyl monomers in aqueous media. The interaction between the oxidizing and reducing agent proceeds with the formation of free radical mechanism. A study of the kinetics of polymerization by thiourea and Ce (IV) have studied. Various redox systems have used Potassium Persulphate successfully for the polymerization of organic vinyl monomers in aqueous media. In the present article, the potassium Persulphate / thiourea redox system was used to polymerize acrylonitrile and the kinetics of polymerization of the monomer with this redox pair has been studied.
6.2.2 Chemistry of Thiourea.

Thiourea is an organic compound of Carbon, nitrogen, sulfur and hydrogen, with the formula CSN$_2$H$_4$ or (NH$_2$)$_2$CS. It is a versatile reagent in organic synthesis. It is a crystalline solid having melting point 176-178$^0$C. It is fairly soluble in water and alcohol. Thiourea by heating with H$_2$O to 140$^0$C gives back ammonium thiocyanate. An acid or alkali hydrolyses thiourea to H$_2$S, NH$_3$ and CO$_2$. Thiourea, H$_2$N – CS – NH$_2$ is prepared by heating isomeric ammonium thiocyanate NH$_4$CNS (a by product in the wet purification of coal – gas) to 170$^0$C. The cooled residue is extracted with water and crystallized. The equilibrium mixture between 140-189$^0$C contains 25-30% of thiourea.$^{23}$
Thiourea – formaldehyde plastics are most – stable and more water resistant, than the Urea – formaldehyde plastics. Thiourea protects wood, wool and fur from insects. Pentothal an anesthetic is a derivative of thiourea.

Oxidimetric determination of thiourea and its organic derivatives have been reviewed by Sing and Verma. The earliest method for the determination of thiourea is by Nolhard, who titrated its hot ammonium solution with standard silver nitrate using an external end – point method. Maly found that when thiourea is oxidized with permanganate in neutral solutions, urea is formed and nearly all the sulphur is oxidized to H₂SO₄. Thiourea has bitter – tasting, soluble in cold water and alcohol. It is used a photography and photocopying, as a rubber accelerator and as an antithyroid drug in treating hyperthyroidism. It is also known as thiocarbamide.

\[
\text{S} \\
\text{H₂N} \quad \text{NH₂}
\]

Other industrial uses of thiourea include production of flame retardant resins, an auxiliary agent in diazo paper and almost all other types of copy paper. The liquid silver – cleaning product Tarnx is essentially a solution of thiourea.

6.2.3 Kinetics Reviews of Thiourea in Redox systems

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In all initiating systems containing thiourea (I), the redox component is isothiourea (II). Thiols (existing in tautomeric equilibrium with thiourea in an aqueous solution) is the reductant. Hebeish and Co-Workers\textsuperscript{24} have used the potassium bromate – Thiourea redox system for grabbing MMA and methylicryllic acid onto Nylon6. Nayak et al\textsuperscript{25} have reported the graft copolymerization of MMA on to silk using the potassium bromate – thiourea redox system. The graft polymerization of MMA on to silk using the potassium peroxidiphosphate – thiourea redox system has been reported by Nayak; Lenka and Mishra\textsuperscript{26}. Panda et al\textsuperscript{27} have reported the graft copolymerization of MMA on to silk using V\textsuperscript{5+} - thiourea, Ferric Chloride – Thiourea\textsuperscript{28} and H\textsubscript{2}O\textsubscript{2} – thiourea\textsuperscript{29} as redox systems. Nayak and co-workers\textsuperscript{30} has investigated polymerization of acrylonitrile initiated by Cr\textsuperscript{6+} - thiourea. This studies while furnishing interesting information on polymerization kinetics.

Polymerization of acrylonitrile initiated by the Ce\textsuperscript{4+} - thiourea redox system\textsuperscript{31} has been investigated at very low temperature (10\textsuperscript{0}C).

The rate of monomer disappearance is proportional to (monomer concentration\textsuperscript{2}, [thiourea] and [Ceric ion]\textsuperscript{1}. The rate of ceric disappearance is proportional to the Ceric and thiourea concentrations, but independent of monomer concentration. A kinetic scheme has been proposed.

Potassium persulphate – thiourea\textsuperscript{32} redox couple has been employed to graft PMMA on to wool in the presence of air under different reaction conditions; graft copolymers were characterized by scanning electron micrographs, thermogravimetry, etc. The effect of additives on graft copolymerization has been studied and a suitable reaction mechanism has been proposed.

Graft copolymerization of MMA onto cellulose with V\textsuperscript{5+} - thiourea redox system\textsuperscript{33} was studied by varying the monomer, initiator, thiourea, acid concentrations and temperature. The graft yield increased with an increase in monomer concentration. The graft yield increased with an increase in thiourea
and acid concentration. Graft copolymerization of MMA onto silk using peroxoypophosphate – thiourea redox system\textsuperscript{34} was studied at 50\textdegree{}C. The rate of grafting was determined by changing [monomer] [thiourea], [initiator], acidity of the medium and temperature. The graft yield increases with an increase of [thiourea]. A measurable increase in graft yield was observed with an increase in acidity of the medium.

Polymerization of MMA with H\textsubscript{2}O\textsubscript{2} – thiourea redox initiator system\textsuperscript{35}. Initiation of polymerization of MMA styrene and acrylonitrile with the redox system Fe\textsuperscript{3+}– thiourea\textsuperscript{36}, has been examined. For the hetero phase polymerization any of the ferric salts, such as FeCl\textsubscript{3}, Fe(SO\textsubscript{4})\textsubscript{2} and Fe(ClO\textsubscript{4})\textsubscript{3} can be used as oxidant, but there is no polymerization in the homogeneous phase when FeCl\textsubscript{3} is used as oxidant.

It was also observed that Fe(ClO\textsubscript{4})\textsubscript{3} retards the radical polymerization of styrene. Though this salt has hardly may any effect on the radical polymerization of MMA. Further, the reaction between Fe (ClO\textsubscript{4})\textsubscript{3} and thiourea was found to be kinetically of second order.

The interaction of MMA with wool under the catalytic influence of the H\textsubscript{2}O\textsubscript{2} – thiourea redox system\textsuperscript{37}, was studied under a variety of conditions. The degree of grafting depends upon the method employed; it is advantageous to first immerse wool in thiourea solution, monomer and H\textsubscript{2}O\textsubscript{2} being then subsequently applied. Increasing the H\textsubscript{2}O\textsubscript{2} concentration is found to be enhancement in the graft yield.

Graft copolymerization of 2 – acrylamido – 2 – methyl – 1 – propane sulphonic acid onto carboxymethyl glucose using potassium bromate / thiourea redox system\textsuperscript{38}, under the inert atmosphere at 40\textdegree{}C, graft yield increases with an increase of thiourea, acid concentration.
EXPERIMENTAL

6.2.4 Materials and Methods

Acrylonitrile (S.D. Fine chem., India) was washed with 5% NaOH followed by dilute orthophosphoric acid and finally with distilled water. It was dried over anhydrous calcium chloride and distilled under reduced pressure of nitrogen atmosphere. The middle fraction was collected and stored at 50°C. All other chemicals such as potassium persulphate, sulphuric acid, thiourea, methanol, ethanol, DMF, cetyl trimethylammonium bromide, and triton x-100 were of analytical grade. A solution of potassium persulphate was prepared by triple distilled water and standardized with standard sodium thiosulphate solution using starch as an indicator. Triple distilled water was used throughout the experiment, pure nitrogen obtained by passing through a column of Fieser’s solution and distilled water, was used for the deaeration condition of all experimental systems.

6.2.5 Kinetic Measurements

Reactions were performed under nitrogen atmosphere in pyrex glass vessels. In a typical kinetic measurements a mixture of solutions containing requisite amounts of inhibitor-free acrylonitrile (0.607M) monomer [M], thiourea [TU] (1.0 X 10^{-2} mol / dm^3), acid (4.0 X 10^{-3}) and H_2O (to keep the total volume constant) were taken in reaction vessels and thermostated at 50°C. The system was flushed with oxygen-free nitrogen for about 20-30 min to expel the dissolved oxygen. At the end of the duration, potassium persulphate solution (4.0 X 10^{-3} mol / dm^3) was added to the reaction vessels and shaken well. The reaction vessel was then sealed with rubber gasket to ensure inert atmosphere. The polymerization starts without any induction period. After about 60 min the reaction was arrested at desired intervals of times by adding a known amount of...
ferrous sulphate solution or by cooling the reaction mixture to 0\(^\circ\) C. The polyacrylonitrile was filtered from the reaction mixture using funnels, washed several times with distilled H\(_2\)O and dried at 70\(^\circ\)C to a constant weight. Finally the rate of polymerization (Rp) was determined gravimetrically\(^{40}\) and potassium persulphate disappearance (-Rm) was also measured.

### 6.2.6 Molecular Weight Determination

The molecular weight M\(_v\) of the purified sample of polyacrylonitrile product was determined by viscometry method. A 1\% solution of the polymer in DMF was filtered through fitted glass filter and placed in an Ubbelhode type suspended level dilution viscometer. The intrinsic viscosity (\(\eta\)) for the reaction mixture was determined and M\(_v\) values were calculated using Mark-Houvink equation given by Stockmayer and Cleland\(^{41}\): \(\eta/\eta_0 = (3.335 \times 10^{-4}) \times M_v^{0.72}\) at 30\(^\circ\)C for polyacrylonitrile in DMF. The molecular weight of the polymer product under standard conditions was found to be 5.81\times 10^4. It increases with monomer concentration and decreases with increase in [potassium persulphate], [thiourea] or temperature. This effect is attributed to the fact that increases in [potassium persulphate], [thiourea] or temperature, provides more chances for premature termination of growing chain polymer radicals, thus reducing the degree of polymerization. Behari et.al.,\(^{42,43}\) have reported similar effects. Density and refractive index determined using the density bottle and Abbe’s Refractometer (1.261 & 1.433) respectively.

### 6.2.7 Results and Discussion

Under the conditions of high temperature (40\(^\circ\)C) it was found that there was no polymerization of the monomer even after 75 min with potassium persulphate alone was used as an initiator. But with potassium persulphate-thiourea as redox initiator, it was noticed that the polymerization reaction proceeded without any induction period. The Steady State was attained within
75 min. The polymerization of acrylonitrile initiated by potassium persulphate-thiourea redox system takes place at a measurable rate in the temperature range 40-80°C. The rate of potassium persulphate disappearance (-Rm) was found to be independent for potassium persulphate at standard concentration. A plot of (-Rm) versus [potassium persulphate] was linear and passed through the origin. A plot of -1/Rm versus 1/[thiourea] was linear with an intercept on the rate axis, indicating Line weaver-Burk kinetics for complex formation.

6.2.8 Rate of polymerization

The rate of polymerization (Rp) increases with the increase of monomer concentration (0.151-1.518M). A plot of log Rp versus log [M] was a straight line with a slope equal to one or unity. (Fig. 1), and a plot of log Rp versus log [M] was a straight line with zero intercept indicating that the order with respect to [monomer] was unity. Rp increases linearly with increase in the thiourea concentration up to [1.0-5.0 x 10^{-2} M]. A plot of log Rp versus log [thiourea] was a straight line passing through the origin (Fig 2). This showed that the order with respect to [thiourea] is 0.42. A regular increase in Rp was also noticed with the increase in [potassium persulphate] [4.0-20.0. x 10^{-3} M]. A plot of log Rp versus log [potassium persulphate] was linear, having a slope of 0.45 with zero intercept (Fig 3), indicating that the order with respect to [potassium persulphate] is fractional. These observations suggest that the termination of polymerization may be caused by the mutual combination of growing polymer radicals.\textsuperscript{44}

The rate of potassium persulphate disappearance (-Rm) was first order with respect to potassium persulphate and is independent of acrylonitrile concentration. It depends on [potassium persulphate] and [thiourea]. A plot of – 1/ R_m versus 1/[thiourea] is Linewear-Burk kinetics for complex formation.\textsuperscript{45}
6.2.9 Reaction mechanism and rate law

The polymerization of acrylonitrile (AN) in aqueous medium is initiated by potassium persulphate-thiourea redox system shows characteristic features of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts because of the insolubility of the polymer (PAN) in the aqueous media. From the kinetic results, a reaction has been proposed involving the initiation by organic free radicals generated by the interaction by the potassium persulphate [PS (II)] with the NH₂

\[ \text{Initiation:} \quad k_i \]
\[ \text{M} + \text{R}^\bullet \quad \rightarrow \quad \text{RM}^\bullet \]

\[ \text{Propagation} \]
\[ \text{RM}^\bullet + \text{M} \quad \rightarrow \quad \text{RM M}^\bullet \]
\[ \text{RM}^{x-1}\text{M} \quad \rightarrow \quad \text{RM}_x\text{M}^\bullet \]
Termination

\[ \text{RM}^* + \text{RM}^* \rightarrow \text{Polymer} \]

Applying steady state approximation

\[- \frac{d}{dt} [R^*] = kd[\text{complex}] - kt[M][R^*] = 0\]

\[ K = [\text{complex}] / [\text{TU}][\text{PS (II)}] \]

\[ [\text{Complex}] = k [\text{TU}][\text{PS (II)}] \]

\[ k_d k[\text{TU}][\text{PS (II)}] - k_i[M][R^*] = 0 \]

\[ [R^*] = k_d k[\text{PS (II)}][\text{TU}] / k_i[M] \]

\[ k_i[R^*][M] = -k_i[\text{RM}^* n][\text{RM}^* n] = k_i[\text{RM}^* n]2 \]

\[ [\text{RM}^* n]2 = (k_i / kt)[R^*][M] \]

\[ [\text{RM}^* n] = (k_i / k_i) \frac{1}{2} [R^*] \frac{1}{2} [M] \frac{1}{2} \]

\[ k_p = [\text{RM}^* n][M] \]

\[ R_p = k_p (k_i / k_i) \frac{1}{2} [R^*] \frac{1}{2} [M] \frac{1}{2} [M] \]

\[ R_p = k_p (k_d k / k_i) \frac{1}{2} [\text{PS (II)}] \frac{1}{2} [\text{TU}] \frac{1}{2} [M] \frac{1}{2} [M] \]

\[ R_p = k_p (k_d k / k_i) \frac{1}{2} [\text{PS (II)}] \frac{1}{2} [\text{TU}] \frac{1}{2} [M] \frac{1}{2} [M] \]

Thus the dependence of \( R_p \) on \([M] [\text{PS (II)}]\) and \([\text{TU}]\) all of which are observed, are consistent with the experimental results. The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence of the existence of transient radical intermediates generated in redox reactions. It also enables the identification of these radicals as end groups of the polymer. Further work on the kinetics of polymerization, various vinyl monomers initiated by the reaction of PS (II) and other transition metals ions, with suitable reductants is in progress in our laboratory.
6.2.10 Dependence on monomer concentration

The rate of polymerization increases with increasing monomer concentration. The order of the reaction with respect of monomer concentration is calculated from the plot of log Rp versus log [M] (Fig 1 and Table I). The order with respect to acrylonitrile concentration is found to be unity in the range of 0.1518-1.5188 mol / dm$^3$. At higher [AN] the rate decreases, because of increase in viscosity of the medium due to the solubility of the polymer in the monomer, rendering the diffusion of the ions difficult through the medium. An order of the reaction higher than unity is indicative of the occurrence of cage effect.\textsuperscript{46}

6.2.11 Rate dependence on [potassium persulphate]  

Rate of polymerization increases with increase in the concentration of potassium persulphate it is due to increases in the concentration of active species. The order of the reaction with respect to potassium persulphate is found to be fractional order in the concentration range 4.0 X 10$^{-3}$–20.0 X 10$^{-3}$ mol / dm$^3$. This is also clearly indicates that the termination occurs through unimolecular interaction of growing polymer chain radical. The molecular weight (Mv) of polyacrylonitrile decreases with increases in [potassium persulphate] (Fig 3 and Table I). This can be explained by the fact that increasing in [potassium persulphate] provides more chances for premature termination growing chain radicals, which reduce the degree of polymerization.\textsuperscript{47}

6.2.12 Rate dependence on thiourea concentration

The increase of thiourea concentration, increase the Rp and reaches optimum level and then it is decreasing gradually. The exponent (slope) of the thiourea was found to be fractional order (0.42) from the plot of log Rp versus log [thiourea] in the concentration range of 1.0 X 10$^{-2}$–5.0 x 10$^{-2}$ mol/ dm$^3$ (Fig
2 and Table I). At higher concentration of thiourea the rate decreases due to the chain transfer or mutual interaction of the growing polymer chain radicals.

6.2.13 Rate dependence on H$_2$SO$_4$ concentration

The kinetic measurements were performed in H$_2$SO$_4$ aqueous solution of different ion concentration. The rate of polymerization (Rp) decreases with an increase in [H$^+$]ion, indicates that the hydrolyzed species of Potassium Persulphate is more reactive than the unhydrolysed species and also that the unprotonated form of thiourea is more reactive than the protonated form. The order with respect to H$^+$ ion concentration was found to be inverse fractional order from the plots of log Rp versus log [H$^+$]. (Fig 4 and Table I).

6.2.14 Rate dependence on Temperature

When temperature of reaction mixture is increased from 40-80°C, the initial rate of polymerization (Rp) and % conversion was increases and beyond 80°C fall in the initial rate & limiting conversion is observed. The observed increase is due to fact that, with increase in temperature, the rate of active center formation increases, which consequently increases the initial rate and conversion with temperature. Further, beyond 80°C decreases the initial rate and limiting conversion. The overall energy of activation (Ea) has been calculated from the Arrhenius plot of log Rp versus 1/T (Fig 5 and Table I) in the temperature range of 40-80°C. Activation energy (Ea) = 18.64 kJ / mole. The other activation parameters calculated from the Eyring plot are as follows: $\Delta H^\ddagger = 16.03$ kJ / mole, $\Delta S^\ddagger = -192 \text{ JK}^{-1} / \text{mole}$, and $\Delta G^\ddagger = 80.66$ kJ / mole,

6.2.15 Rate dependence on organic Solvents

1) Since the properties of a polymer mostly depend on the nature of the medium, various water–miscible organic solvents such as methanol, DMF and ethanol have been observed their effect on the rate of polymerization
When added to the reaction mixture in equal volume (5%v/v) a depression in the initial rate of polymerization and the limiting conversion has been observed. The increasing order of depression by these solvents is methanol < ethanol < DMF.

2) The cause of depression in the rate of polymerization and % conversion by the added organic solvents may be explained.

3) When the organic solvents are added to the reaction mixture, they cause a decrease in the area of shielding of a strong hydration layer in aqueous medium, which results in the termination of radical end of the growing chain.

4) Some amount of catalyst may be consumed in the oxidation of these organic solvents due to which the concentration of catalyst decreases and a depression in rate is observed. The sluggish radicals thus produced may not be equally capable of initiating the polymerization.

6.2.16 Rate dependence on surfactants

Addition of anionic surfactant, sodium lauryl sulfate (SLS) increases the Rp above and below the CMC value. The cationic surfactant cetyltrimethyl ammonium bromide (CTABr) is increasing the rate above and below CMC value. In contact, nonionic surfactants like triton x-100 have no effect on the rate of polymerization. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization.\cite{48}

6.2.17 Conclusions

Acrylonitrile is polymerized in a nitrogen atmosphere by the redox system of Potassium Persulphate / thiourea via a free radical mechanism. The polymerization reaction with respect to monomer concentration is 1.0. And the
reaction order related to the Potassium Persulphate and thiourea concentrations are 0.45 and 0.42 respectively, which indicates that bimolecular mechanism is suggested and the following rate equation is derived:

\[ V_p = k[M]^{1.0} [\text{potassium persulphate}]^{0.45} [\text{thiourea}]^{0.42} \]

From the Arrhenius plot, the overall energy of activation (Ea) has been calculated as 18.64 kJ / mol in the investigated range of temperatures.
Table: 1. Effect of variations of [PS (II)], [TU], [Monomer] and Temperature on the rate of polymerization

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Figure 1 Effect of [monomer] on the rate of Polymerization,

\[
[\text{PS(II)}] = 4.0 \times 10^{-3} \text{ mol / dm}^3, \quad [\text{TU}] = 1.0 \times 10^{-2} \text{ mol / dm}^3,
\]

\[
[\text{Monomer}] = (0.1518 - 1.5188) \times 10^{-2} \text{ mol / dm}^3,
\]

Temperature = 323 K. \([\text{H}_2\text{SO}_4]\) = (2.0 \times 10^{-3} \text{ mol / dm}^3),
Figure 2 Effect of [Thiourea] on the rate of Polymerization.

\[ \text{[PS(II)]} = 4.0 \times 10^{-3} \text{ mol / dm}^3, \text{[TU]} = 1.0-5.0 \times 10^{-2} \text{ mol / dm}^3 \]

\[ \text{[Monomer]} = 0.6075 \times 10^{-2} \text{ mol / dm}^3, \text{Temperature} = 323 \text{ K.} \]

\[ \text{[H}_2\text{SO}_4] = (2.0 \times 10^{-3} \text{ mol / dm}^3), \]
The rate of Polymerization,

$[\text{PS(II)}] = 4.0-20.0 \times 10^{-3} \text{ mol / dm}^3$, $[\text{TU}] = 1.0 \times 10^{-2} \text{ mol / dm}^3$, $[\text{Monomer}] = 0.0675 \times 10^{-2} \text{ mol / dm}^3$, Temperature = 323 K.

$[\text{H}_2\text{SO}_4] = (2.0 \times 10^{-3} \text{ mol / dm}^3)$,
Figure 4 Effect of H$_2$SO$_4$ on the rate of Polymerization,

\[ 3 + \log[H^+] \]

[PS(II)] = 4.0-20.0 x $10^{-3}$ mol / dm$^3$, [TU] = 1.0 x $10^{-2}$ mol / dm$^3$, [Monomer] = 0.0675 x $10^{-2}$ mol / dm$^3$, [H$_2$SO$_4$] = (2.0-10.0) x $10^{-3}$ mol / dm$^3$), Temperature = 323 K.

Figure 5 Effect of temperature on the rate of Polymerization,

[PS(II)] = 4.0-20.0 x $10^{-3}$ mol / dm$^3$, [TU] = 1.0 x $10^{-2}$ mol / dm$^3$, [Monomer] = 0.0675 x $10^{-2}$ mol / dm$^3$, Temperature = 313-353 K.

[\(H_2SO_4\)] = (2.0 x $10^{-3}$ mol / dm$^3$),
Fig: 6. IR SPECTRA OF POTASSIUM PERSULPHATE- THIOUREA ACRYLONITRILE REDOX SYSTEM
REFERENCES

Conclusion

Kinetics of polymerization is a center of attraction both to an academician as well as to an industrialist; it provides an insight to the invisible molecular transformation mechanism and the same time method of regulating the reaction rate so that the reaction span and quality of the polymer can be turned to the needed parameters.

Though the kinetics of redox polymerization of vinyl monomers has been extensively studied, the review of literature shows that there is still scope for further study. Although radiation induced polymerization is the clean method of polymerization, it has the disadvantage that the radiation may damage the polymer products. The redox polymerization has several advantages. The polymerization can be carryout at low temperature and relatively high molecular weight polymers with the high yield can be obtained in a short period. The redox polymerization further provides direct experimental evidence of the existence of transient radical intermediates generated in situ in redox reactions, and enables identification of these radicals as end groups of polymers, throwing new light on the mechanism of redox reactions. The structure of monomer and arrangement of their double bounds can also be studied. Finally we conclude that the Ce(IV)-Tartaric acid redox system was very good and CAT-H₂O₂ also having good yield and Rp.
SCOPE FOR THE FURTHER WORK

In these redox systems studying further works as follows:

1) To study of other parameters, like conductivity, Ultrasonic Interferometer-ray diffraction Scanning Electron Microscopy to the polymer products.
2) Use of other reluctant for the study of polymerization of vinyl Monomers.
3) Other oxidants also used to study of polymerization of vinyl Monomers.
4) Use the other vinyl monomers for the study of redox polymerization.
5) Study of grafting in redox system to be proposed.
6) Study of applications in different fields for redox polymerization products.
7) Calculate the degree of dissociation constant.
8) Calculate the number of molecules having monomer.
9) Determination of degree of polymerization.
10) Calculating the reductants efficiency.
11) Calculating the repeating units of polymer or Chain length of the polymer.
12) Determination of termination by coupling or termination by disproportionation.
13) Determination of molecular weight by other methods.
14) Calculating the polydispersity on polymer surface.