Polymerization kinetics of acrylonitrile initiated by K$_2$S$_2$O$_8$-Ag$^+$-EDTA redox system

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Received 18 November 1999; revised 30 April 2001

The kinetics of polymerization of acrylonitrile has been studied employing K$_2$S$_2$O$_8$-EDTA-Ag$^+$ redox couple under atmospheric oxygen. The rate expression $R_p \alpha [\text{Monomer}]^{0.45} [\text{K}_2\text{S}_2\text{O}_8]^{0.42} [\text{Ag}^+]^{0.46} \cdot \text{EDTA}^{0.80}$ has been obtained and a plausible mechanism suggested to explain the experimental findings. The effect of varying concentrations of monomer and redox components, temperature, added salts, solvents, H$^+$ ions and surfactants on the polymerization kinetics have also been studied.

Materials and Methods
Acrylonitrile (Loba Chemie, India) was made inhibitor-free by washing it several times initially with 10% NaOH and then with 2N sulphuric acid, followed by distilled water. Potassium persulphate (Loba Chemie, India) was used as received. Silver nitrate was of B.D.H. grade and used without further treatment. All solutions used were prepared in doubly distilled water.

The polymerization was carried out in an oxygen atmosphere using the conventional gravimetric method and the percent conversion of monomer to the polymer was calculated by the formula adopted in our previous work$^8$.

Results and Discussion
A stepwise plausible mechanism for the polymerization of acrylonitrile by the K$_2$S$_2$O$_8$-Ag$^+$-EDTA redox couple may be outlined as below:

(a) Formation of free radicals

\[
\text{S}_2\text{O}_8^{2-} + \text{Ag}^+ \xrightarrow{k_1} \text{SO}_4^{-} + \text{SO}_4^{2-} + \text{Ag}^{2+} \quad \ldots (1)
\]

\[
\text{Ag}^{2+} + \text{EDTA} \xrightarrow{k_2} \left[\text{Ag}^{2+} \cdot \text{EDTA}\right] \text{complex} \quad \ldots (2)
\]

\[
\left[\text{Ag}^{2+} \cdot \text{EDTA}\right] \xrightarrow{k_3} \text{Ag}^+ + \text{EDTA}^{-} + \text{H}^+ \quad \ldots (3)
\]

\[
\text{S}_2\text{O}_8^{2-} + \text{EDTA} \xrightarrow{k_4} 2\text{SO}_4^{2-} + \text{EDTA}^{-} + \text{H}^+ \quad \ldots (4)
\]

\[
\text{Ag}^{2+} + \text{M} \xrightarrow{k_5} \text{M} + \text{Ag}^+ \quad \ldots (5)
\]

where EDTA$^-$ = R$^-$ = CH$_2$CH$_2$N

\[
\text{CH}_2
\]

\[
\text{CH}_3
\]

\[
\text{CH}_2
\]

\[
\text{CH}_3
\]

\[
\text{NH}_2
\]

\[
\text{CH}_2
\]

\[
\text{H}_2\text{CO}_2\text{H}
\]

and X = CH$_2$CO$_2$H

(b) Initiation

\[
\text{R} + \text{M} \xrightarrow{k} \text{RM} \quad \ldots (6)
\]

(c) Propagation

\[
\text{RM} + \text{M} \xrightarrow{k} \text{RM}_1 \quad \ldots (7)
\]

\[
\text{RM}_n + \text{M} \xrightarrow{k} \text{RM}_{n+1} \quad \ldots (7)
\]
(d) Termination

\[ R\text{M}_n + R\text{M}_m \xrightarrow{k_1} \text{Polymer} \quad \cdots (8) \]

In addition to the above bimolecular termination, unimolecular termination can also take place following any of the suggested mechanisms as given below:

(i) By electron transfer

In this type of termination, the growing macroradicals transfer its electrons to the metal ion, \[ R\text{M}_n + \text{Ag}^{2+} \xrightarrow{k_i} \text{Polymer} + \text{Ag}^+ \quad \cdots (9) \]

(ii) By dissolved impurity

Dissolved metal ion impurity may also cause termination of growing macroradicals, as shown below:

\[ RM_n = \text{Metal ion impurity} \xrightarrow{k} RM_n \quad \cdots (10) \]

As an approximation the overall rate of polymerization may be expressed as

\[ R_p = k_p [M][RM_n] \quad \cdots (11) \]

Now, from the steady state assumption, we can write

Rate of initiation = Rate of termination

or

\[ k_p [R][M] = k_p [RM_n]^2 \quad \text{Therefore,} \]

\[ [RM_n] = \left( \frac{k_p}{k_i} \right)^{1/2} [R]^{1/2} [M]^{1/2} \quad \cdots (12) \]

Substituting eq(16) in eq(14), we get

\[ k_p [S_2O_8^{2-}][Ag^+] + k_i [Ag^{2+}][EDTA] + k_i [S_2O_8^{2-}][EDTA] - k_p [R][M] = 0 \quad \cdots (14) \]

Since \[ Ag^{2+} \] ions are transient species, their concentration can be determined by steady state treatments, i.e.,

\[ \frac{d}{dt} [Ag^{2+}] = 0 \]

\[ k_i [S_2O_8^{2-}][Ag^+] - k_i [Ag^{2+}][EDTA] + k_i [S_2O_8^{2-}][EDTA] - k_p [R][M] = 0 \]

Again using steady state assumption for the complex \[ [Ag^{2+} - EDTA] \], we can write

\[ k_i [S_2O_8^{2-}][Ag^+] = k_i [Ag^{2+}][EDTA] + k_i [S_2O_8^{2-}][EDTA] - k_p [R][M] = 0 \]

\[ [Ag^{2+}][EDTA] = \frac{k_i [S_2O_8^{2-}][Ag^+]}{k_p [M]} \quad \cdots (15) \]

Since \[ [M] >> [EDTA] \], we can write,

\[ [Ag^{2+}] = \frac{k_i [S_2O_8^{2-}][Ag^+]}{k_p [M]} \quad \cdots (16) \]

Substituting eq.(16) in eq.(14), we get

\[ k_i [S_2O_8^{2-}][Ag^+] + k_i [Ag^{2+}][S_2O_8^{2-}][EDTA] + k_i [S_2O_8^{2-}][EDTA] - k_i [R][M] = 0 \]

\[ [Ag^{2+}][S_2O_8^{2-}][EDTA] = \left( \frac{k_i [S_2O_8^{2-}][Ag^+]}{k_p [M]} + k_i [Ag^{2+}][S_2O_8^{2-}][EDTA] - k_i [R][M] = 0 \]

\[ k_i [S_2O_8^{2-}][EDTA] - k_i [R][M] = 0 \]

\[ [R] = \frac{k_i [S_2O_8^{2-}][EDTA]}{k_i [M]} \quad \cdots (17) \]

Now, from eq.(17) and (13), we get

\[ R_p = k_c \left( \frac{k_i [S_2O_8^{2-}][EDTA]}{[M]} \right)^{1/2} \]

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\[ \frac{[Ag^{2+}][S_2O_8^{2-}][EDTA]}{[M]} \quad \cdots (18) \]

Obviously \[ R_p d[M]^{1/2} [Ag^+]^{1/2} \quad \cdots (19) \]

The observed rate expression is in full agreement with our experimental findings to be discussed in forthcoming sections.

Persulphate effect (Initiator)

When the concentration of initiator (persulphate) varies from 1.0 to 5.0 x 10^{-2} mol dm^{-3} both the initial rate of polymerization and percentage conversion are found to increase (Fig. 1). The observed increase is due to the fact that the rate of free radical generation (eq. 1 and 4) becomes faster, therefore, initial rate and percentage conversion increase.

In a polymerization study by Guichhait et al., the monomer assisted decomposition of persulphate was investigated in the presence of methacrylonitrile (MAN) and found that rates of persulphate decomposition increased with increase in monomer concentration. It was also found that in absence of
monomer the rate of persulphate decomposition was independent of time. The authors also postulated a plausible mechanism for the monomer assisted decomposition. The idea of monomer dependent decomposition was also supported by Dunn who accounted the following two steps for the observed decomposition.

\[
\begin{align*}
S\text{O}_4^- + M(= RH) &\rightarrow HSO_3^- + R \\
R + S\text{O}_4^{2-} &\rightarrow R - O - SO_3^- + SO_4^{2-}
\end{align*}
\]

From the double logarithmic plot, the exponent with respect to the initiator was found to be 0.42 which is less than the expected 0.5 order. The half order dependence normally confirms a bimolecular terminated polymerization mechanism and a value in between 0.5 and unity implies a mixed termination, i.e., a bimolecular and metal ion caused unimolecular termination.

In the present case a lower exponent than 0.5 may be attributed to primary radical termination. As observed in the present case the order with respect to metal ion exceeds than that with respect to initiator, i.e., persulphate. Similar type of findings were also reported by Hariharan and Meenakshi, who investigated polymerization of acrylonitrile initiated by persulphate and Cu\textsuperscript{2+} system. In their study they also observed that rate of polymerization was 0.5 order dependent on metal ion while zero order with respect to the catalyst (initiator). They attributed this unusualness due to the following reasons:

1. The radical production does not involve both the components of redox system.
2. Either persulphate or metal ion is involved in complexation with the monomer.
3. The initiation by metal ion or SO\textsuperscript{4}\textsuperscript{-} is faster as compared to that by other species. However, a linear termination mechanism was proposed as predominant reaction.

As mentioned earlier the 0.42 order with respect to persulphate could be accounted for the occurrence of primary radical termination of following type:

\[
\begin{align*}
SO_4^2^- + Ag^+ &\rightarrow SO_3^- + Ag^{2+} \\
EDTA + Ag^+ &\rightarrow EDTA + Ag^{2+}
\end{align*}
\]

**Ag\textsuperscript{+} effect**

When the concentration of AgNO\textsubscript{3} is raised in the range 0.5 \times 10^{-3} to 3.0 \times 10^{-2} mol dm\textsuperscript{-3}, both initial rate and limiting conversion increase. The increase in initial rate may be due to the formation of larger number of initiating free radicals because their generation is governed by the amount of catalyst available in the system to participate in redox reaction. As from the double logarithmic plot, the order with respect to Ag\textsuperscript{+} ion was found to be 0.46 and this nearly half order dependence of metal ion has also been reported by several workers.

We have also carried out polymerization in the absence of Ag\textsuperscript{+} and found that almost no detectable polymer was formed even after two hours.

**Monomer effect**

The variation of initial rate of polymerization and limiting conversion with increasing concentration of monomer has been studied. The rate of polymerization and percentage conversion were found to increase with increasing concentration of acrylonitrile in the range 12.1 to 160.7 \times 10^{-2} mol dm\textsuperscript{-3}. The increase may be due to the availability of larger number of monomer molecules in propagation step which consequently results in observed findings.

From the double logarithmic plot the order with respect to monomer has been calculated to be 0.45 which is slightly smaller than the observed half value. The smaller value of exponent may be attributed to reasons that monomer may also form a charge transfer complex with the oxygen of the persulphate so that the reactivity of the monomer is suppressed. This suppressed reactivity results in a lower order dependence on monomer concentration. The monomer exponent normally varies from one to more than one. However, less than one value have also been
of the components of redox system, therefore, its role is quite significant. The effect of EDTA has been studied by varying [EDTA] in the range $1.0 \times 10^{-3}$ to $5 \times 10^{-3}$ mol dm$^{-3}$. It is found that both initial rate and limiting conversion increases (Fig. 2) but beyond the concentration $5 \times 10^{-2}$ mol dm$^{-3}$ EDTA initial rate decreases (not shown in Fig. 2). The increase observed in initial rate and limiting conversion in the initial concentration range may be attributed to the fact that with increase in [EDTA], greater number of initiating free radicals will be produced in step (iii) and as a consequence, initial rate and limiting conversion will increase.

The order in EDTA was found to be 0.80 as calculated from the double logarithmic plot which is greater than the expected half value. The higher exponent with respect to activator may be explained due to the termination of primary radicals. In a similar type of redox system consisting of persulphate and polyamine for the polymerization of acrylonitrile, the order in polyamine was also found to be 0.77 (Ref. 18).

It was also observed that at higher concentration of [EDTA], both the polymerization rate and percentage conversion fall. This fall in rate may be due to the cage effect$^{19}$ which is a characteristic phenomenon in heterogeneous polymerization systems.

Organic solvent effect

The presence of organic solvents in free radical initiated polymerization systems affects not only the kinetic features but also the stereoregularity of the end product$^{20}$. Normally, the polymerization kinetics slows down in the presence of organic solvents, however, in the present case the addition of organic solvents such as water miscible alcohols to the reaction system (5% v/v) has resulted in an increase in the polymerization rate and percent conversion. The order of increasing initial polymerization rate and percent conversion was found as follows:

$H_2O < BuOH < MeOH < EtOH < n-PrOH$

The reason for the observed increase may be that the added alcohols, due to their oxidation, form alkoxy radicals which can further initiate the polymerization due to formation of free radicals. A very interesting observation was noted by Santappa and co-workers$^{21}$ in the kinetics of polymerization initiated by chromic acid - reducing agents ($n$-butanol, ethylene glycol). It was observed that the percentage conversion to polymer was appreciable with acrylonitrile monomer and very small with monomers such as methyl acrylate and acrylamide under similar conditions.

**EDTA effect**

In the present study, EDTA has been taken as one of the components of redox system, therefore, its role....

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**Fig. 2** — Time versus conversion curve for varying EDTA concentration at fixed [Monomer] = 0.80 mol dm$^{-3}$, [Persulphate] = $3 \times 10^{-2}$ mol dm$^{-3}$, [Ag$^+$] = $1 \times 10^{-3}$ mol dm$^{-3}$; Temp. = 32 ± 0.02°C. The order in EDTA was found to be 0.80 as calculated from the double logarithmic plot which is greater than the expected half value. The higher exponent with respect to activator may be explained due to the termination of primary radicals. In a similar type of redox system consisting of persulphate and polyamine for the polymerization of acrylonitrile, the order in polyamine was also found to be 0.77 (Ref. 18).

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conditions. Methanol was found to react with peroxodisulphate,

\[
\begin{align*}
S_2O_8^{2-} + CH_3OH & \rightarrow SO_4^- + HSO_4^- + CH_2OH \\
CH_3OH + SO_4^2- & \rightarrow HSO_4^- + CH_2OH \\
CH_3OH + S_2O_8^{2-} & \rightarrow HSO_4^- + SO_4^- + CH_2O \\
CH_2OH + CH_2OH & \rightarrow CH_3OH + HCHO
\end{align*}
\]

Generally, the retardation effect by organic solvents is seen in vinyl polymerization which is due to the transfer of macroradical chains to the solvent resulting in the formation of low molecular weight polymers. However, in the present case, no such chain transfer has been observed which is further supported by the evidence that the molecular weight of resulting polyacrylonitrile increases on solvent addition. With increasing in number of carbon atoms in the alkyl chain, the molecular weight also increases in the order: \(H_2O < MeOH < EtOH < PrOH < BuOH\).

**Inorganic salt effect**

The effect of cations and anions on the kinetics of polymerization has been studied by addition of equimolar (0.01M) concentration of inorganic salts to the reaction medium. In order to study anionic effect, salts of potassium were added to the medium. The results indicate that the initial rate and limiting conversion decrease with \(SO_4^{2-}\) and \(NO_3^-\) but in the case of \(PO_4^{3-}\) both initial rate and percent conversion increases, \(PO_4^{3-} > \text{Without salt} > NO_3^- > SO_4^{2-}\).

The reason for observed decrease may be given below as:

1. The added anions cause a change in the ionic strength of the medium that results in a change in the ionic strength of the medium. This results in a change in the initial rate and limiting conversion.
2. The added anions may also cause a screening of coulombic forces between reacting ions which as a consequence offer the rates of radical generation steps.

The influence of addition of cation on the initial rate and limiting conversion has been investigated by adding alkali metal ion (0.01M) to polymerization system. The results obtained imply that added cations brings about a depression in the initial rate and limiting conversion in the case of \(Na^+\) and \(K^+\), but in the case of \(Li^+\) both initial rate and percent conversion increase. The polymerization rate and limiting conversion decrease in the order \(Li^+ > \text{without salt} > Na^+ > K^+\). The reason for observed decrease may be that the added cations cause a termination of growing macroradicals. In the case of addition of \(Li^+\) ions, the observed increase in \(Li_2SO_4\) brings about an increase in both the rate and maximum polymerization. The promoting action may be due to some facile reaction path through the intermediary of the redox system formed by the added metal ion.

**Dielectric constant effect**

The effect of varying dielectric constant of the medium on polymerization kinetics has been investigated by adding varying amounts of dioxane to the reaction medium. The results obtained indicate that with increasing proportion of dioxane in the reaction medium, the initial rate of polymerization and percentage conversion increase. The reason for the observed increase may be due to the formation of greater number of initiating free radicals as dioxane can also act as initiation by forming dioxyl radicals.

**Dioxane + Ag$^+ \rightarrow Ag^{2+} + \text{dioxyl radical (R)}$**

\[Ag^{2+} + R M_n \rightarrow Ag^{+} + \text{Polymer}\]

where \(R = \)

**pH effect**

The role of pH is quite significant in solution polymerization. The pH may affect the rate of polymerization either by coagulating the dispersed phase and/or by affecting the rate of initiating process. In the present case at pH 4.62, polymerization occurs while above and below this pH, i.e., at 2.0, 7.0 and 11.3 very low polymerization takes place. The reason may be that peroxydisulphate initiated polymerization is adversely affected by the presence of acid in the reaction medium due to decomposition of \(K_2S_2O_8\) into non-free radical products.

\[S_2O_8^{2-} + H^+ \rightarrow SO_4^- + HSO_4^-\]

**Surfactant effect**

In the present case, the effects of anionic (sodium oleate) and cationic surfactant on the course of polymerization have been investigated by adding sodium oleate and CTAB to reaction mixture at, below and above CMC values. The results obtained indicate a fall in the initial rate and per cent conversion which may be explained by the fact that due to the binding of \(Ag^+\) ions to anionic end of surfactant the rate of generation of initiating free
radicals is suppressed which consequently results in a decrease in the initial rate and percent conversion.

In the case of cationic surfactant the formation of insoluble complex between cationic surfactant and $S_2O_2^-$ ions results in a decrease in the initial rate and per cent conversion. Alexander et al\textsuperscript{24} also reported the formation of an insoluble complex between cationic surfactant and $S_2O_2^-$ ions only above CMC.

**Temperature effect**

The effect of temperature on the kinetics of polymerization has been investigated by varying the temperature of medium in the range 10\textdegree\textsuperscript{C} to 50\textdegree\textsuperscript{C}. It has been found that a rise in temperature of the solution causes initial polymerization rate and percentage conversion to increase because of the reason that at higher temperature the rate of active centre formation also increases which as a consequence increases the rate of polymerization. The energy of activation as calculated from Arrhenius plot was found to be 1.44 KJ/mol which favours the present experimental findings.

**References**