Chain initiation in persulphate initiated aqueous polymerization of methacrylonitrile under inert atmosphere and mechanism of persulphate decomposition

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It has been found that the initial rate of persulphate decomposition in the persulphate concentration range of 0.40 x 10^{-2} to 3.00 x 10^{-2} mol dm^{-3} and the monomer, methacrylonitrile (MAN), concentration range of 0.16 to 0.40 mol dm^{-3} may be given by the following expression,

$$-d[S_2O_8^{2-}] \propto [\text{MAN}]^{3.35 \pm 0.05} \times [S_2O_8^{2-}]^{1.17 \pm 0.05}$$

A reaction scheme has been suggested to explain the kinetic data.

In the persulphate initiated aqueous and emulsion polymerization of vinyl monomers, the chain initiation is suggested to occur by a mechanism shown in Scheme 1 (see refs. 1-5).

(A) $S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^-$
(B) $SO_4^- + H_2O \rightarrow HSO_4^- + OH$
(C) $2OH^- \rightarrow H_2O_2$ (or $H_2O + 1/2 O_2$)
(D) $SO_4^- + M \rightarrow M_j (= O_3-S-O-M)$
(E) $M_j + M \rightarrow M_{j+1}$
(F) $2M_j \rightarrow $ Polymer

Scheme 1

Such a mechanism predicts that the rate of persulphate decomposition would be independent of [monomer] and also on the nature of the monomer. However, this contention is not found valid. Dunn has suggested that induced decomposition of persulphate may occur by steps (G) and (H).

(G) $SO_4^- + M (= RH) \rightarrow HSO_4^- + \cdot R$
(H) $\cdot R + S_2O_8^{2-} \rightarrow R-O-SO_3^- + SO_4^-$

Dunn's mechanism predicts that pH of aqueous solution will decrease with increase in [monomer] but this was not supported by experimental facts. While studying the emulsion polymerization of vinyl acetate initiated by persulphate, Chang suggested that the $\cdot R$ radicals are produced from the chain transfer reactions taking place in the latex particles.

Being very small in size, $\cdot R$ radicals would diffuse into the aqueous phase to cause further induced decomposition. If all the $\cdot R$ radicals thus are oxidised by persulphate ions in the aqueous phase, then there would be no polymerization at higher [persulphate]. Sarkar et al. studied the aqueous polymerization of vinyl acetate and found that at higher [persulphate] (> 10^{-2} mol dm^{-3}) the polymerization does occur but the polymers so obtained are partly insoluble in common solvents namely benzene, acetone, etc. This of course indicates that at higher [persulphate] the polymerization reaction mechanism is very complex and probably cross-linked polymer would form. Since very little work has been done on the aqueous and emulsion polymerization of methacrylonitrile (MAN), initiated by potassium persulphate, we report herein the mode of chain initiation of aqueous polymerization of MAN and the mode of persulphate decomposition.

Materials and Methods

Purification and processing of reagents have been described elsewhere in detail. Potassium persulphate (GR, E Merck) was recrystallised three times from doubly distilled water. Methacrylonitrile (MAN) (AG, Fluka; stabilised by hydroquinone) was washed with 1% NaOH, followed by distilled water till free of alkali and dried over anhydrous calcium chloride. It was distilled under reduced pressure and vacuum fractionated, and the middle fraction (refractive index = 1.401 at 25°C) was collected and stored at -5°C. Before use the monomer was tested for the presence of peroxide. If peroxide was
detected, the monomer was refluxed under nitrogen atmosphere and distilled before use. The reaction was carried out in a hermetically sealed pyrex flask fitted with a Hg-seal stirrer and connectors for passing nitrogen and for extracting solutions. It was noted that the aqueous solution of MAN did not alter the pH of the distilled water (6.9-7.0 at 25°C). During the reaction at 50°C samples were collected at different times and quenched immediately in ice. The pH of the solution was measured at room temperature (25 ± 3°C). Persulphate was estimated by the method of Kolthoff and Carr. Percentage conversion of monomer to polymer was estimated gravimetrically. Polymer molecular weight \( M_n \) was measured viscometrically in DMF solvent at 30°C using Mark-Houwnik’s equation, \[ [\eta] = 0.36 \ (M_n)^{0.503} \] where \([\eta]\) is in ml/gm and \(\eta_0/C = \eta_0/\eta\) + \(K_h[\eta]^{1.2}C\), the Huggin’s constant \(K_h\) was found to be 0.366, \(C\) is the concentration of polymer in DMF in g/100 ml.

**Results**

The results of persulphate decomposition in the presence of MAN are shown in Figs 1 to 4 and Table 1. It is found that the rates of persulphate decomposition increase with increase in [monomer]. Initial rates of persulphate decomposition were estimated at various [monomer] and at a given [persulphate], by plotting the time average rates of persulphate decomposition as a function of time and extrapolating the resulting linear plot to zero time (Fig. 1) to get the initial rate at zero time. It is also found that in the absence of monomer, the rate of persulphate decomposition is independent of time (Fig. 1, curve, E) in the early stages of the reaction, whereas in the presence of monomer the rates of decomposition were decreased with time and with the conversion of monomer to polymer (Fig. 1). Initial rates of persulphate decomposition were also determined by the tangent method of Hinshelwood and

![Fig. 1](image1.png)

**Fig. 1**—Average rates of persulphate decomposition at various concentrations of the monomer (MAN) and at a given concentration of persulphate \(2.0 \times 10^{-2} \text{ mol dm}^{-3}\), (A) 0.40, (B) 0.30, (C) 0.24, (D) 0.16, (E) 0.00 (mol dm\(^{-3}\)) of the monomer (MAN). It is assumed that the extrapolated rates at zero time are the initial rates at various concentration of the monomer (MAN).

![Fig. 2](image2.png)

**Fig. 2**—Order plot for the monomer with respect to the persulphate decomposition log (initial rate of persulphate decomposition, in mol dm\(^{-3}\) s\(^{-1}\)) versus log (initial monomer concentration, in mol dm\(^{-3}\)) has been plotted. The slope of the line 1.38 ± 0.05, gives the order of the monomer.

![Fig. 3](image3.png)

**Fig. 3**—Effect of [monomer] on the pH change of the aqueous solutions of persulphate \(0.50 \times 10^{-2} \text{ mol dm}^{-3}\) during its decomposition at 50°C. pH was measured at 25°C: (A) persulphate alone, (B) persulphate and monomer \(0.12 \text{ mol dm}^{-3}\), (C) persulphate and monomer \(0.24 \text{ mol dm}^{-3}\), (D) persulphate and monomer \(0.48 \text{ mol dm}^{-3}\).
the rates obtained by the two different methods agree within ±10.0%. The order in [monomer] was found to be 1.38 ± 0.05. Fig. 2 shows the time average rates of persulphate decomposition at various [persulphate] and at a given [monomer]. From the initial rates the order in [persulphate] was found to be about 1.17.

Fig. 3 shows the pH variations with time during the reaction in the presence and absence of monomer. The pH of the persulphate solution decreased rapidly initially, and then slowly with time. Increase in [MAN] in the solution reduced the rate at which pH decreased, but the pH change (i.e. ∆pH) was not zero in this system even when the solution was saturated with monomer (4.0% v/v, at 50°C), whereas ∆pH was almost zero in the persulphate-acrylonitrile system containing 8.5% acrylonitrile (w/v). It is found that the monomer injected late in a run accelerated the rates of persulphate decomposition (Fig. 4), indicating that the monomer in the aqueous phase is interacting with the S₂O₅²⁻ ions.

Data in Table 1 show the conversion of monomer to polymer with time in the aqueous polymerization of MAN. The viscosity average molecular weight (\( \bar{M}_v \)) of the polymer was of the order of \( 10^5 \). The Huggin's constant \( (K_H) \) in DMF was 0.366 at 30°C. The latex particles were found unstable in the presence of higher [persulphate] \( (1.0 \times 10^{-2} \text{ mol dm}^{-3}) \). We did not investigate here the polymer end groups, because it is well known that in the persulphate initiated polymerization of vinyl monomers, end groups are hydroxyl and sulphate\(^+\).

### Table 1 — Molecular weights and colloidal stability of polymers in the latex solution

<table>
<thead>
<tr>
<th>Reaction time (min.)</th>
<th>Conversion (%) of monomer to polymer</th>
<th>Colloidal stability (MgSO₄/dm³)</th>
<th>[( \eta )] ( \times 10^{-2} )</th>
<th>( \bar{M}_v ) ( \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>6.65</td>
<td>62.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>90</td>
<td>10.53</td>
<td>66.6</td>
<td>1.59</td>
<td>2.49</td>
</tr>
<tr>
<td>120</td>
<td>13.36</td>
<td>60.24</td>
<td>1.66</td>
<td>2.73</td>
</tr>
<tr>
<td>135</td>
<td>15.65</td>
<td>57.80</td>
<td>1.63</td>
<td>2.62</td>
</tr>
<tr>
<td>165</td>
<td>18.28</td>
<td>53.20</td>
<td>1.56</td>
<td>2.42</td>
</tr>
</tbody>
</table>

### Discussion

The simple mechanism (see Scheme 1) of persulphate decomposition in the presence of a vinyl monomer predicts that the rate of persulphate decomposition should be independent of [monomer]. This is in contrast to the result obtained presently. We propose Scheme 2 to account for the results obtained in this investigation.

\[
\text{S}_2\text{O}_5^{2-} \rightarrow 2\text{S}_2\text{O}_4^{2-} \quad \text{in the aqueous phase} \quad \ldots (1)
\]

\[
\text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4^{-} + \text{OH} \quad \text{in the aqueous phase} \quad \ldots (2)
\]

\[
2\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad \text{or} \quad \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad \text{in the aqueous phase} \quad \ldots (3)
\]

\[
\text{S}_2\text{O}_4^{2-} + \text{M} \rightarrow \text{M}_1 \quad \text{[= O}_3\text{S} - \text{O} - \text{CH}_2 - \text{C}(\text{CH}_3)\text{CN]} \quad \text{in the aqueous phase} \quad \ldots (4)
\]

\[
\text{S}_2\text{O}_4^{2-} + \text{M} \rightarrow (\text{M}_1)_j \quad \text{[= CCH}_2 \text{- C}(\text{CH}_3)(\text{CN}) - \text{OSO}_2\text{]} \quad \text{in the aqueous phase} \quad \ldots (4a)
\]

\[
\text{S}_2\text{O}_4^{2-} + \text{M} \rightarrow \text{HSO}_4^{-} + \text{CH} = \text{C}(\text{CH}_3) - \text{CN} \quad \text{or} \quad \text{CH} = \text{C}(\text{CH}_2) - \text{CN} \quad \text{in the aqueous phase} \quad \ldots (4b)
\]

\[
\text{S}_2\text{O}_5^{2-} + \text{M} \rightarrow \text{M}_1 + \text{S}_2\text{O}_4^{2-} \quad \text{in the aqueous phase} \quad \ldots (5)
\]

\[
\text{M}_j + \text{M}(= \text{RH}) \rightarrow \text{M}_j\text{H} + \text{R} \quad \text{in water, in the particle} \quad \ldots (6)
\]

\[
\text{M}_j + \text{M} \rightarrow k \quad \text{M}_{j+1} \quad \ldots (7)
\]

\[
(M)_{(j)} \Rightarrow (M)_{(j)} \quad \text{in the particle-water interface and where} \quad j = 1 \text{ to } 10 \quad \ldots (8)
\]
\[
\begin{align*}
& (\dot{M}_i)_w + P \text{ (dead particle)} \rightleftharpoons P^* \text{ (active particle)} \quad \ldots (9) \\
& (\dot{M}_i)_w + S_2O_8^{2-} \rightarrow (M_j - O - SO_3^2)^*_w + SO_4^- \text{ in water,} \quad \ldots (10) \\
& (M)_w \rightleftharpoons (M)_p \text{ at the particle water interface} \quad \ldots (11) \\
& 2(\dot{M}_i)_w \xrightarrow{k^w} \text{Polymer in water} \quad \ldots (12) \\
& 2(\dot{M}_i)_p \xrightarrow{k_p} \text{Polymer in a latex particle or between two active particles if they coagulate together; } i = 1 \text{ to any value, say 1000 or more} \ldots (13)
\end{align*}
\]

Scheme 2

In the absence of monomer, SO$_4^-$ primary free radicals are produced only in reaction (1) and would disappear via reaction (2), and so the solution would be acidic. pH of the solution would decrease with time which is consistent with the results shown in Fig. 3. In the presence of monomer, SO$_4^-$ radicals are also produced via the reactions (5) and (10), and disappear via steps (2), (4) and (4a). If the monomer is highly reactive towards SO$_4^-$ radicals, and where SO$_4^-$ addition to the olefinic double bond of the monomer is not hindered due to the steric effect of the adjacent alkyl groups viz. CH$_3$, C$_2$H$_5$, C$_6$H$_5$ etc., then almost all SO$_4^-$ radicals would disappear via step (4), as was found in the persulphate-acrylonitrile system. In the latter system, the pH of the medium did not alter when the aqueous solution was saturated with the monomer. In the presence of monomer, SO$_4^-$ radicals are also produced via the reactions (5) and (10), and disappear via steps (2), (4) and (4a). If the monomer is highly reactive towards SO$_4^-$ radicals, and where SO$_4^-$ addition to the olefinic double bond of the monomer is not hindered due to the steric effect of the adjacent alkyl groups viz. CH$_3$, C$_2$H$_5$, C$_6$H$_5$ etc., then almost all SO$_4^-$ radicals would disappear via step (4), as was found in the persulphate-acrylonitrile system.$^8$ In the latter system, the pH of the medium did not alter when the aqueous solution was saturated with the monomer.$^9$ In the MAN-persulphate system however, slight change in pH even when the aqueous solution was saturated with MAN (Fig. 3) indicates that either reaction (2) or (4b) or both are occurring. It seems to us that because of the steric effect of the CH$_2$ group in MAN, reaction (4a) is unlikely to occur. Reaction (4b) requires higher activation energy.$^{14}$ and hence may not be important here at low temperature$^{13}$ (50°C). It appears that even when the solution was saturated with MAN, reaction (2) was not totally suppressed, since SO$_4^-$ radicals do not react with MAN vigorously.$^{15}$

From the data shown in Fig. 1, the first order rate constant ($k_1$) of the reaction (1), viz. S$_2$O$_8^{2-}$ $\rightarrow$ 2SO$_4^-$, was found to be $1.71 \times 10^{-6}$ s$^{-1}$, which agrees with the literature values$^4$, viz. (1.3 to 2.61) $\times$ $10^{-6}$ s$^{-1}$ at 50°C. In our measurement we found that $k_1$ was independent of pH in the pH range of 4 to 7, while Kolthoff et al.$^{16}$ and Wilmarth et al.$^5$ reported that $k_1$ was almost independent of pH in the pH range of 3 to 13. Below pH = 3 and above 13, $k_1$ was found to increase rapidly at a given temperature.$^{4,5,18}$ Only Breuer and Jenkins$^{18}$ reported that $k_1$ was pH dependent, and the maximum value of $k_1$ ($= 2.8 \times 10^{-6}$ s$^{-1}$) was observed at pH 7 and 50°C. Such a high value of $k_1$ was not reported by any other worker.$^3$-$^5$. Since the order in [monomer] is not zero, it seems that there are other reactions which would account for the higher rates of persulphate decomposition in the presence of the monomer.

The most plausible reactions which seem to reflect the effect of varying [monomer] are reactions (5) and (10), in which S$_2$O$_8^{2-}$ ions interact with the monomer directly and also with the water soluble monomeric free radicals, viz. M$_j$ [= O - S - O - CH$_2$ - C(CH$_3$) - CN] and R[= CH$_3$ = C(CH$_2$) - CN or CH$_3$ - C(= CH$_2$) - CN] which are resonating structures. For simple kinetic treatment, it is assumed that M$_j$ and R are indistinguishable. It follows from the Scheme 2 that

\[
-\frac{d[S_2O_8^{2-}]}{dt} = k_1[S_2O_8^{2-}] + k_5[S_2O_8^{2-}][M] + k_{10} (M)_w [S_2O_8^{2-}] \ldots (14)
\]

Rate of initiation in the aqueous phase $(R)_w$, is given by

\[
(R)_w = 2k_1[S_2O_8^{2-}] + k_5[M][S_2O_8^{2-}] + k_{10} (M)_w [S_2O_8^{2-}]V_w \ldots (15)
\]

where $V_w$ is the volume fraction of water, $V_p$ is the volume fraction of polymer, so that $V_w + V_p = 1.0$. Assuming (1) and (5) are major chain initiating reactions, and neglecting (10), we get,

\[
(R)_w = 2k_1 + 2k_5[M] [S_2O_8^{2-}]V_w \ldots (16)
\]

Under our experimental conditions, $V_w \gg V_p$ and so here $V_w \approx 1.0$.

Rate of termination in the aqueous phase $(R(t))_w$, is given by

\[
(R(t))_w = 2k_{tw} (M)_w [S_2O_8^{2-}]V_w \ldots (17)
\]

In the steady state, $(R)_w = (R(t))_w$, and hence

\[
(M)_w = k_{-0.5} (k_1 + k_5[M])^{0.5} [S_2O_8^{2-}]^{-0.5} \ldots (18)
\]

Combining (14) and (18), we get

\[
\frac{1}{[S_2O_8^{2-}]} \frac{d[S_2O_8^{2-}]}{dt} = (k_1 + k_5[M]) + k_{10} k_{tw}^{-0.5} \times (k_1 + k_5[M])^{0.5} [S_2O_8^{2-}]^{-0.5} \ldots (19)
\]
Hence a plot of left hand side of Eq. (19) versus $[S_2O_5^{2-}]^{-0.5}$ should be linear at a given [monomer] (Fig. 5). From the slope and the intercept of such a plot, $k_s$ and $k_{10}$ have been estimated, taking $k_1 = 1.71 \times 10^{-6}$ s$^{-1}$ and $k_{10} = 7.32 \times 10^9$ (dm$^3$.mol$^{-1}$.s$^{-1}$) from Dainton $et$ $al.$ for the aqueous polymerization of acrylonitrile. Since $k_{10}$ for the aqueous polymerization of MAN is not known. The [monomer] was 0.36 (mol dm$^{-3}$) from Dainton's $et$ $al.$ and $k_s = 1.12 \times 10^{-5}$ (dm$^3$.mol$^{-1}$.s$^{-1}$) and $k_{10} = 1.46 \times 10^3$ (dm$^3$.mol$^{-1}$.s$^{-1}$). It may be pointed out here that Dainton's $k_s$ and $k_{10}$ for the aqueous polymerization of acrylonitrile have been questioned by McCarthy $et$ $al.$ who believe that Dainton's $k_s$ and $k_{10}$ values were very high.

Fig. 4 shows that the monomer injected late in a run increased the rate of persulphate decomposition pointing to a crucial role of monomer in persulphate decomposition in the aqueous phase. Since in a given run, the rate of persulphate decomposition was found decrease continuously with time (Fig. 1) or with the conversion of monomer to polymer, it is clear that the polymer in the latex particles was not responsible for the induced decomposition of persulphate in this system. Further, the polymer was found to be soluble in DMF indicating that no crosslinked polymer was formed during the reaction. In the vinyl acetate-persulphate and methyl acrylate-persulphate systems, it was observed$^{21}$ that the monomer injected late in a run had no measurable effect on the rates of persulphate decomposition, it is believed that these monomers are good solvents for their respective polymers, and so they are quickly absorbed by the existing latex particles in the system, and very little of the injected monomer remains in the aqueous phase. For MAN, the distribution coefficient (i.e. concentration of monomer in the polymer phase/concentration of monomer in the aqueous phase at 50°C) is very low (about 1.80), whereas that of vinyl acetate or methyl acrylate is very high$^{21}$, viz. about 22.0 $\pm$ 2.0.

The data in Table 1 show that the rate of polymerization is very slow and the total conversion in 165 mins is also very small, viz. only about 18%. It seems that the locus of polymerization was shifted overwhelmingly from the aqueous phase to the surface of the latex particles, where polymerization occurred at slow rate due to the relatively low [monomer] at the reaction site, even though the polymerization occurred at an accelerated rate. The colloidal stability of the latex particles was found to decrease with time, which indicates that incipient coagulation of the latex particles was taking place during the reactions. Molecular weight of polymer was found to increase with time in the early stages of the reaction, attain a maximum and then decrease with time. This observation is probably associated with the change of polymerization rates with time. Similar observation were noted in the emulsion polymerization of styrene$^{22}$ and also in the aqueous and emulsion polymerizations of methyl acrylate$^{23}$ and of ethyl acrylate.

Conclusion

The data presented here show clearly that the major initiation reactions in the persulphate-water-MAN system are reactions (1) and (5). In fact, at a [monomer] of 0.30 mol dm$^{-3}$, $k_1 = 1.71 \times 10^{-6}$s$^{-1}$, $k_s = 1.12 \times 10^{-5}$ dm$^3$.mol$^{-1}$.s$^{-1}$ and at $[K_2S_2O_8] = 10^{-3}$mol dm$^{-3}$, we find that

$$\frac{[R_1]}{[R_5]} = \frac{2k_s[M][S_2O_5^{2-}]}{2k_1[S_2O_5^{2-}]} = \frac{1.12 \times 10^{-5} \times 0.3}{1.71 \times 10^{-6}} = 2.0$$

i.e. the rate of initiation ($R_1$) due to step (5) is twice that due to step (1). Kinetic analysis also suggests that a part of the water soluble radicals are oxidised by the persulphate ions in the aqueous phase.

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References

21 Guchhait S, Sarkar S, Banerjee M & Konar R S, (To be published).