Aqueous polymerization of methyl methacrylate initiated by manganese (III) pyrophosphate - potassium thiocyanate redox system: A kinetic study

B S Sherigara, S K Rai & K Shivakumar

4Department of Post-graduate Studies in Industrial Chemistry, Karnataka University, Dharwad, India
3Department of Polymer Science, Sir M.V. Post-graduate Centre, Mandya, University of Mysore, India.
2National College of Pharmacy, Shimoga 577 201, India.

Received 11 May 2000; revised 26 September 2000

Aqueous free radical polymerization of methyl methacrylate monomer [M], initiated by manganese (III) pyrophosphate - potassium thiocyanate redox system, has been studied in the pH range 2-3 and in the temperature range 25-40°C at constant ionic strength. The rates of polymerization (Rp) and manganese (III) disappearance have been measured. The effects of certain salts, water miscible organic solvents, and surfactants on the rate of polymerization have been investigated. The temperature dependence of the rate has been studied and the activation parameters computed using the Arrhenius plot. A polymerization mechanism, involving chain initiation by radicals derived from decomposition of manganese (III)-thiocyanate complex formed in situ and bimolecular chain termination, is suggested. The rate of polymerization is found to be proportional to \([M]^1\), \([\text{Mn(III)}]^1\), \([\text{H}^+]^1\), \([\text{NCS}^-]^1\), \([\text{Mn(II)}]^1\), \([\text{P}_2\text{O}_7^{4-}]^1\). The overall energy of activation in the range studied (25-40°C) is found to be 32.2 kJ mol\(^{-1}\).

Redox initiation of polymerization of vinyl monomers in the presence of high valent transition metal ions like Co(III), Ce(IV), Cr(VI), Mn(III), V(V) etc. can be used to throw light on the mechanistic details of the elementary steps in the redox process\(^1\).

Manganese (III) pyrophosphate has been found to be a selective oxidant for several types of inorganic\(^{10,11}\) and organic compounds\(^{12-15}\). Reactions involving thiocyanate are of interest due to their analytical, biological and industrial applications\(^16\). The kinetics of oxidation of thiocyanate ion by manganese (III) pyrophosphate has recently been investigated\(^17\) by our group. As an initiator, manganese(III)-thiocyanate redox system has certain advantages: Polymerization proceeds by measurable rate at room temperature, and no induction period is observed under deaerated condition. Manganese(III) pyrophosphate can function as a moderate oxidant over a wide range of pH (1 to 6). The steady state is attained within 60 min. This redox system has low energy of activation indicating higher efficiency. As a part of our research programme on the polymerization by chemical and electrochemical methods\(^18\) using Mn(III) and Ti(III), we are reporting herein the results of our study on polymerization of methyl methacrylate initiated by manganese (III) pyrophosphate-thiocyanate redox system in aqueous medium.

Materials and Methods

Preparation of reagents

Methyl methacrylate (SISCO-CHEM, India) was freed from inhibitor by washing with 5% NaOH, followed by washing with dilute H\(_2\)SO\(_4\) and finally with distilled water. The washed monomer was dried over anhydrous sodium sulphate, distilled under reduced pressure and the middle fraction was collected and stored at 5°C.

A solution of manganese (III) pyrophosphate was prepared by the method of Belcher and West\(^10\). It was standardized by iodometry, the value was further checked by titrating against standard ferrous ammonium sulphate using barium diphenylamine sulphonate as internal indicator. KNCS solution was standardized argentometrically\(^19\). All other chemicals used were of analytical grade and were used without further purification. Doubly distilled water was used throughout. Nitrogen used for the deaeration of
The equation relating the intrinsic viscosity \( [\eta] \) to degree of polymerization \( (P_n) \) employed was:

\[
\log P_n = 3.342 + 1.13 \log [\eta]
\]

(for PMMA in benzene at 30°C)

**Results and Discussion**

Methyl methacrylate was polymerized in aqueous medium in the pH range 2-3 at 25-40°C in the presence of the redox system manganese(III)pyrophosphate-thiocyanate. There was some induction period under undeaeated conditions and, the induction period become negligible under deaerated condition. Further on adding benzoquinone no polymerization was noticed. Thus, it was evident that the polymerization was initiated by free radicals formed *in situ* by the redox system. The steady state was attained within 60 min.

**Rate of Mn\(^{3+}\) disappearance**

The rate of disappearance of Mn\(^{3+}\), \( (-R_m) \) was first order in [Mn\(^{3+}\)] and independent of [monomer]. The plot of \( (-d[Mn^{3+}] / dt)^{-1} \) versus [NCS]\(^{-1} \) was linear with an intercept on the rate axis showing Lineweaver-Burk kinetics\(^2\) for complex formation.

![Fig. 1](image-url)
The polymerization reaction is enhanced by increase in both [H+] and ionic strength (I). The increase in \( R_p \) with increase in the ionic strength by adding sodium perchlorate may be understood in terms of the salt catalyzing the propagation step.19 The separating polymer phase remains in aqueous solution as a stable colloid or precipitate depending upon the ionic strength of the medium. The colloidal polymer has a tendency to form gel and viscosity of the medium increases resulting in gel effect.20

**Effect of monomer (M) concentration on the rate of polymerization**

The rate of polymerization, \( R_p \), was found to increase linearly with increase in [monomer] in the range (0.0375-0.1875 mol dm\(^{-3}\)). The order in [monomer] was found to be 1.2 from the plot of log \( R_p \) versus log [M] (Fig. 2a). An order of value higher than one implies gel or occlusion phenomenon. But at concentrations above 0.1875 mol dm\(^{-3}\) the rate of polymerization decreases. This may be due to the fact that the unreacted monomer solvates the polymer. This increases the viscosity of the medium and decreases the diffusion of the reacting species and hence decreases the rate of polymerization.21

**Effect of initiator concentration on the rate of polymerization**

The rate of polymerization, \( R_p \), increases with increase in \([\text{Mn}^{3+}]\) in the range (7.4 x 10\(^{-3}\) - 20 x 10\(^{-2}\) mol dm\(^{-3}\)) which may be due to increase in the concentration of free radicals and the exponent of \([\text{Mn}^{3+}]\) has been found to be half from a plot of log \( R_p \) versus log \([\text{Mn}^{3+}]\) (Fig. 3a) which clearly indicates that termination occurs through bimolecular interaction of growing polymer chain radicals.22

**Effect of thiocyanate ion concentration on the rate of polymerization**

Effect of thiocyanate ion concentration on the rate of polymerization was studied by varying the [NCS\(^{-}\)] in the range (0.6 x 10\(^{-3}\) - 1.8 x 10\(^{-2}\) mol dm\(^{-3}\)). The rate of polymerization was found to increase with increase in [NCS\(^{-}\)] and the order in [NCS\(^{-}\)] was found to be 0.5 from the plot of log \( R_p \) versus log [NCS\(^{-}\)]. A plausible explanation for this observation can be advanced by assuming that the reaction is initiated by the free radicals produced by the interaction of \( \text{Mn}^{3+} \) with NCS\(^{-}\) ion. The production of these radicals is facilitated at higher concentration of NCS\(^{-}\) ion, thus accounting for the increase in the rate of polymerization (Fig. 3b).
Effect of pH on the rate of polymerization

The pH of the reaction mixture was varied between 2-3 by varying phosphoric acid concentration. The rates of polymerization and percentage conversion were found to increase with a decrease in pH. The effect of pH on the rate of polymerization may be due to coagulation of the dispersed phase and/or variation in the rate of the initiating process. It may also be due to alternation of redox potentials of either or both the components of the redox system. But below pH 2.5 there is a decrease in the rate of polymerization. This may be due to the fact that below pH 2.5, the rate of oxidation of thiocyanate becomes faster in comparison with the rate of polymerization as pointed out by Nayak et al. The order of the reaction in $[H^+]$ was found to be 0.5 from the plot of $\log R_p$ versus $\log [H^+]$ (Fig. 1b).

Effect of Mn$^{2+}$ and P$_2$O$_7^{4-}$ on the rate of polymerization

Manganese(II) is the reduced product of the oxidant Mn$^{3+}$. The retardation of one electron manganese(III) oxidation of various reductant by added Mn$^{2+}$ is a common feature of the Mn$^{3+}$/Mn$^{2+}$ redox system. One possible explanation for this effect is the reversible disproportionation equilibrium,

$$2\text{Mn}^{3+} \leftrightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$$

The rate of polymerization and percentage conversion decreases regularly with the increase in [Mn$^{2+}$] and [P$_2$O$_7^{4-}$] and the order in each was found to be -0.5.

Effect of organic solvents on the rate of polymerization

The initial rate of polymerization and molecular weight of the polymer decreases, when water miscible organic solvents are added in equal proportion (5% v/v) (Fig. 4). The decrease was found to be in the order: MeOH < EtOH < isopropanol. The mechanism of retardation by these solvents, may be due to the chain transfer phenomenon, i.e. abstraction of hydrogen atom by the propagating macro radical, resulting in the formation of alkoxy radical as shown below:

$$\text{R-OH} + \text{RMn}^* \rightarrow \text{R-O}. + \text{RMnH}$$

(polymer product)

The stability of the resulting alkoxy radical (R-O.) decides the retarding efficiency of these solvents. The chain transfer taking place by the solvent R-OH is supported by the IR spectrum indicating the $\geq$C-O-R as end group of methyl methacrylate macromolecule.

The other causes of retardation in the initial rate of polymerization are (i) the organic solvents in the reaction medium decreases the area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the radical end of growing chain and (ii) some amount of catalyst may be consumed in the oxidation of these solvents, which reduces the concentration of catalyst and thus suppresses the rate of polymerization.

The molecular weights of the resulting PMMA samples in different solvents have been determined and are found to be isopropanol, 21,300; ethanol,
Effect of surfactants on the rate of polymerization

The rate of polymerization was also studied in the presence of certain anionic, cationic and non-ionic surfactants. Cationic micelles of cetyltrimethyl ammonium bromide accelerates the rate and anionic micelles of sodium lauryl sulphate retard the rate, and a non-ionic surfactant, Triton-x-100 has no effect. The catalysis of the rate of polymerization by cationic micelles can be explained on the assumption that the thiocyanate ion, when incorporated by the cationic micelles of CTABr, is in an electrostatically favourable environment for attack by Mn(III) species and hence the formation of free radicals occurs more easily, as a result of which the rate of polymerization increases. Thiocyanate anion cannot be easily incorporated as micelles of anionic nature and remains mostly in solution, whereas the manganese (III) species are kept away from the reaction site, as they are bound to the micelles.

Effect of variation of temperature on the rate of polymerization

The rate of polymerization and percentage conversion increases steadily with increase in temperature. The activation energy calculated from the Arrhenius plot of log $R_p$ versus $1/T$ in the temperature range 25-40°C was found to be 32.2 kJ mol$^{-1}$ (Fig 2b). The overall thermodynamic parameters calculated were: $\Delta H^\circ = 34.076$ kJ mol$^{-1}$; $\Delta G^\circ = 79.62$ kJ mol$^{-1}$ and $\Delta S^\circ = -152.85$ JK$^{-1}$ mol$^{-1}$.

Reaction mechanism and rate law

The polymerization of methyl methacrylate in aqueous medium initiated by Mn$^{3+}$ ion in the presence of thiocyanate ion has the characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before the initiation of polymerization, becomes heterogeneous as soon as polymerization starts due to the insolubility of the polymer in aqueous phase.

From the proportionalties obtained between the measurable parameters and variables, Scheme1 is suggested involving initiation of polymerization by free radicals produced by the interaction of Mn$^{3+}$ with potassium thiocyanate and the termination by disproportionation.

a) Formation of free radicals:

$$NCS^- + H^+ \rightleftharpoons HNCS \quad \cdots (1)$$

$$Mn^{3+} (H_2P_2O_7)^3^- + HNCS \rightleftharpoons Mn^{3+} (H_2P_2O_7)^3^- HNCS \quad \cdots (2)$$

$$X \rightleftharpoons HNCS^2^- + Mn^{3+} (H_2P_2O_7)^2^- + H_2P_2O_7^2^- \quad \cdots (3)$$

$$Y \rightarrow NCS^+ + H^+ \quad \cdots (4)$$

b) Initiation of polymerization:

$$R^* + M \rightarrow RM^* \quad \cdots (6)$$

c) Propagation

$$RM^* + M \rightarrow RM^* \quad \cdots (7)$$

d) Termination

$$RM^* + RM^* \rightarrow Polymer \quad \cdots (8)$$

Scheme1

Applying the steady state principles for all the radicals a rate equation consistent with the present kinetic data can be derived as follows:

$$[X] = \frac{k_1[Mn^{3+}][HNCS] + k_{33}[Y][Mn^{3+}][H_2P_2O_7^{2-}]}{k_{22} + k_{33}} \quad \cdots (9)$$

$$d[Y]/dt = k_3 [X] - k_{23} [Y][Mn^{3+}][H_2P_2O_7^{2-}] - k_4 [Y] = 0 \quad \cdots (10)$$
Substituting for \([X]\) from Eq. (9) we get

\[
[Y] = \frac{k_2k_4 [\text{Mn}^{3+}] [\text{HNCS}]}{[\text{Mn}^{2+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] (k_3 k_2) + k_4 (k_2 + k_3)} \quad \ldots (11)
\]

\[
d[R']/dt = k_4 [Y] - k_5 [R'] - k_1 [R'] [M] = 0 \quad \ldots (12)
\]

Substituting for \([Y]\) in Eq. (12) we get,

\[
[R'] = \frac{k_2k_4 [\text{Mn}^{3+}] [\text{HNCS}]}{(k_2 + k[M]) \{((k_3 + k_2) [\text{Mn}^{3+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] + k_4 (k_2 + k_3)) \ldots (13)
\]

Assuming steady state condition the rate of initiation is equal to the rate of termination.

\[
k_i [R'] [M] = k_i [\text{RM}']^2
\]

\[
[\text{RM}'] = \frac{[k/k_i]^{1/2}[R']^{1/2}[M]^{1/2}}{[k/k_i]^{1/2}[M]^{1/2}((k_3 + k_2) + k_4 (k_2 + k_3)) \ldots (14)
\]

Substituting Eq. (13) in Eq. (14)

\[
[\text{RM}'] = \frac{[k/k_i]^{1/2}[M]^{1/2}((k_3 + k_2) [\text{Mn}^{3+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] + k_4 (k_2 + k_3))}{(k_2 + k[M]) [(k_3 + k_2) [\text{Mn}^{3+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] + k_4 (k_2 + k_3))} \ldots (15)
\]

The rate of polymerization is given by the rate of propagation.

\[
R_p = k_p [\text{RM}'] [M]
\]

Substituting for \([\text{RM}']\) and \([\text{HNCS}]\) we get

\[
R_p = k_p \left( \frac{k_4k_1k_2k_3k_4}{k_i} \right)^{1/2}
\]

\[
\frac{[M]^{1/2} [\text{Mn}^{3+}]^{1/2} [\text{H}^{+}]^{1/2} [\text{NCS}]^{1/2}}{(k_2 + k[M])^{1/2}((k_3 + k_2) [\text{Mn}^{3+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] + k_4 (k_2 + k_3))^{1/2}} \ldots (16)
\]

The rate of \([\text{Mn}^{3+}]\) disappearance is given by the expression

\[
- d[\text{Mn}^{3+}] / dt = -R_m
\]

\[
= \frac{k_1k_2k_3k_4 [\text{Mn}^{3+}] [\text{H}^{+}] [\text{NCS}]}{k_4 (k_2 + k_3) + k_2k_3k_4 [\text{Mn}^{3+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] \ldots (17)
\]

and the kinetic chain length

\[
n = \frac{k_i [M]^{1/2} (k_3 + k [M])^{1/2} [k, k_2 [\text{Mn}^{2+}] [\text{H}_2\text{P}_2\text{O}_7^{2-}] + k_4 (k_2 + k_3))^{1/2}}{(k_2k_3k_4)^{1/2} [\text{Mn}^{3+}]^{1/2} [\text{H}^{+}]^{1/2} [\text{NCS}]^{1/2}}
\]

The dependence of initial rate of polymerization \(R_p\) on \([\text{Mn}^{3+}]^{1/2} [\text{H}^{+}]^{1/2}, \text{[NCS]}^{1/2} [\text{Mn}^{3+}]^{1/2} [\text{Mn}^{3+}]^{1/2}\) and \([\text{P}_2\text{O}_7^{4-}]^{1/2}\) all of which were observed is consistent with Scheme 1. At very low monomer concentration, the factor \((k_3 + k [M])\) reduces to \(k_3\) and hence \(R_p ([M])^{1/2}\). At high monomer concentration, \(k_i [M] >> k_s\) and hence \(R_p \propto [M]\). According to the above equation the possibility of termination by \(\text{Mn(III)}\) is ruled out, and the termination is rather by disproportionation.

The existence of a rigid state, resulting from an associative process, is consistent with the negative \(\Delta S_e\) of reactions of transition metal complexes involving associative mechanism\(^3\). The highly negative \(\Delta S_e\) also suggests that the transition state involves an associated species, formed probably by solvation, responsible for lowering the entropy of the products thereby showing a high negative entropy change, \(\Delta S_e\) and corresponding high value of \(\Delta G_e\). Thus aqueous free radical polymerization provides direct experimental evidence for the existence of transient radical intermediates formed \(\text{in situ}\) by the manganese(III) - KNCNS redox system. This allows the identification of the radicals as end groups of the polymer. The polymer poly(methyl methacrylate) formed gives positive nitrogen and sulphur tests, suggesting NCS as the end group. Further their spectrum shows a CN absorption at 2260 cm\(^{-1}\) and a strong absorption at 1720 cm\(^{-1}\) from a CO\(_2\)Me group, also significant absorptions at about 1150 cm\(^{-1}\) and 1350 cm\(^{-1}\) reveal aliphatic either linkage \(\Sigma(C-O-R)\) at the methyl methacrylate molecular end group originating most likely from the organic solvent, R-O-H.

References
10 Belcher R & West T S, Anal Chim Acta, 6 (1952) 322.
20 Lineweaver H & Burk D, J Am chem Soc, 56 (1934) 658.
30 Misra G S & Rebellow J, J macromolChem, 175, 3117.