Notes to the Editor

Peroxo salts as initiators of vinyl polymerization: 3. Polymerization of methacrylic in acid initiated by perodisulphate ion—pH effect and metal ion catalysis

S. P. Manickam, U. Chandra Singh, K. Venkatarao and N. R. Subbaratnam,
Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625021, India and Institute of Polymer Science, University of Madras, A. C. College Campus, Madras – 600025, India

INTRODUCTION

Our preliminary investigations on the polymerization of methacrylic acid by peroxodisulphate ion revealed very interesting kinetic features[1]. We wanted to investigate further the detailed effect of pH and metal ions Ag^+ and Cu^{2+} on the rate of polymerization. Uncatalysed polymerizations were conducted under acidic and alkaline conditions to detect changes in the mechanism, if any. We present here the results along with the mechanisms proposed.

EXPERIMENTAL

Methacylic acid (Koch-Light Lab., U.K.) was purified by double distillation under reduced pressure over copper powder[2]. Potassium peroxodisulphate (E. Merck G. R) was twice recrystallized from water. $AgClO_4$ was obtained by treating Ag_2CO_3 (prepared from the AnalaR salts of $AgNO_3$ and Na_2CO_3) with perchloric acid (E. Merck G. R.). $Cu(ClO_4)_2$ was prepared from AnalaR $CuCO_3$ and perchloric acid. $NaClO_4$ (E. Merck G.R.) was used as such without further purification. Water. double distilled over alkaline permanganate and deionized, was used to prepare the reagents. The reaction mixture was deaerated by passing oxygen-free nitrogen and the temperature was controlled to ±0.01°C. The rate of polymerization, R_p was measured by estimating the monomer concentration at various times by bromometry[3]. The experiments with $AgClO_4$ were done in the absence of light.

RESULTS AND DISCUSSION

Uncatalysed polymerization in alkaline medium

At a pH of 10.5 where methacrylic acid monomer (pK_a = 4.36) will exist as methacylate anion, R_p depended on $[S_2O_8^{2-}]^{1/2}$ and [M] (*Figure 1*). Experiments at four temperatures gave the overall enthalpy of activation as 18 kcal.mol^{-1} (*Figure 2*). The reaction showed a positive salt effect. The following mechanism will explain all these observations

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot -} \qquad (1)$$

$$SO_4^{\cdot -} + M^- \xrightarrow{k_2} R^{\cdot -} \qquad (2)$$

$$R_{n-1}^{\cdot -} + M^- \xrightarrow{k_{p1}} R_n^{\cdot -} \qquad (3)$$

$$R_n^{\cdot -} + R_m^{\cdot -} \xrightarrow{k_{t1}} \text{Polymer} \qquad (4)$$

$R^{\cdot -}$ is $^-O_4S{-}CH_2{-}\dot{C}(CH_3){-}COO^-$; $R_n^{\cdot -}$ is the polymer radical, $\sim\!\sim\!\sim{-}CH_2{-}\dot{C}(CH_3){-}COO^-$.

Under steady state conditions, assuming 100% efficiency in the initiation process, we get the relation,

$$R_p = \frac{2^{1/2}k_{p1}k_1^{1/2}}{k_{t1}^{1/2}}[S_2O_8^{2-}]^{1/2}[M^-]$$

in agreement with the experimental results. Reactions (2), (3) and (4) involve ions of like charges and hence they will be slow, resulting in a low rate of polymerization. The reaction shows a positive salt effect, which is consistent with

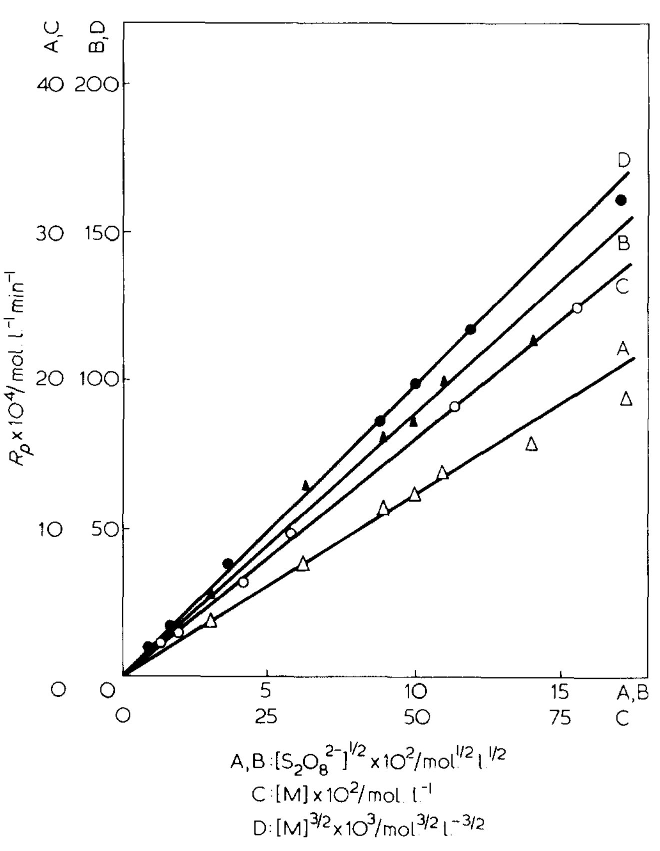

Figure 1 Dependence of R_p on $[S_2O_8^{2-}]^{1/2}$ in the polymerization of methacrylic acid. △, [M] = 0.38 mol.l^{-1}, pH = 10.5; ▲, [M] = 0.124 mol.l^{-1}, [H$^+$] = 0.1 mol.l^{-1} and R_p as a function of [M] in alkaline medium and $[M]^{3/2}$ in acid medium; ○, $[S_2O_8^{2-}]$ = 0.01 mol.l^{-1}, pH = 10.5; ●, $[S_2O_8^{2-}]$ = 0.01 mol.l^{-1} [H$^+$] = 0.1 mol.l^{-1}

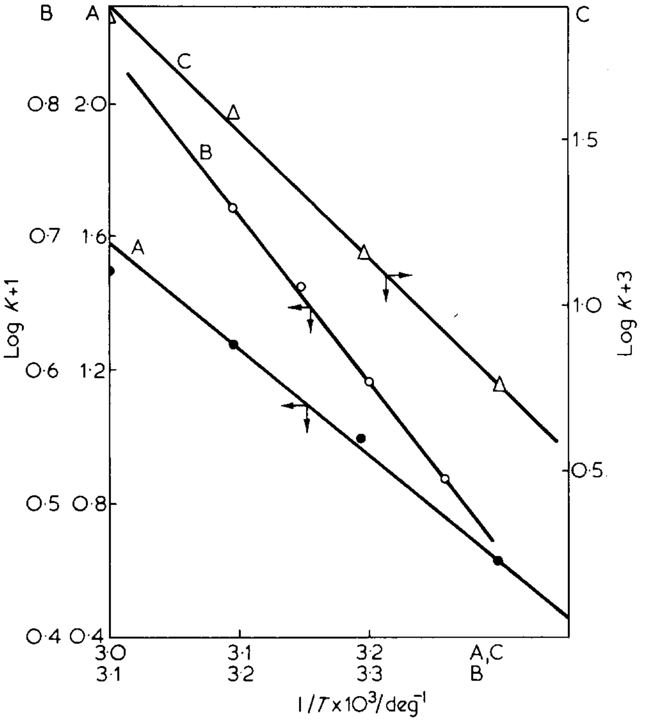

Figure 2 Plot of log k *versus* $1/T$ for the polymerization of methacrylic acid. ●, $[Ag^+] = 0$, $[M] = 0.1252$ mol.l^{-1}, $[S_2O_8^{2-}] = 0.01$ mol.l^{-1} $[H^+] = 0.1$ mol.l^{-1}, $\mu = 1.2$ mol.l^{-1}; ○, $[Ag^+] = 2 \times 10^{-4}$ mol.l^{-1} $[M] = 0.1398$ mol.l^{-1}, $[S_2O_8^{2-}] = 0.004$ mol.l^{-1}. $[H^+] = 0.1$ mol.l^{-1}, $\mu = 0.22$ mol.l^{-1}; △, $[Ag^+] = 0$, $[M] = 0.37$ mol.l^{-1}, $[S_2O_8^{2-}] = 0.01$ mol.l^{-1}, pH = 10.5, $\mu = 1.2$ mol.l^{-1}

the above mechanism. The direct interaction between $S_2O_8^{2-}$ and M^- seems to be less probable, because of steric hindrance caused by the α-methyl group in M^-

Uncatalysed polymerization in acid medium

In acid medium $[HClO_4] = 0.1M$, where methacrylic acid will be in the undissociated state, R_p was proportional to $[S_2O_8^{2-}]^{1/2}$ and $[M]^{3/2}$ (*Figure 1*). The overall enthalpy of activation for the reaction was 12 kcal. mole^{-1} (*Figure 2*). R_p was not sensitive to variation in the ionic strength. The following mechanism is proposed to explain all our kinetic results.

$$S_2O_8^{2-} + M \xrightarrow{k_3} R^{\cdot} + SO_4^{\cdot -} \qquad (5)$$

$$SO_4^{\cdot -} + M \xrightarrow{k_4} R\cdot \qquad (6)$$

$$R_{n-1}^{\cdot} + M \xrightarrow{k_{p2}} R_n^{\cdot} \qquad (7)$$

$$R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_{t2}} \text{Polymer} \qquad (8)$$

Here $R^{\cdot}$ indicates $^-O_4S{-}CH_2{-}\dot{C}(CH_3){-}COOH$; $R_n^{\cdot}$ indicates the polymer radical $\sim\sim\sim{-}CH_2{-}\dot{C}(CH_3){-}COOH$.

Under steady state conditions we get the relation,

$$R_p = \frac{2^{1/2} k_{p2} k_3^{1/2}}{k_{t2}^{1/2}} [S_2O_8^{2-}]^{1/2} [M]^{3/2}$$

in agreement with our experimental results. The reactions (5) to (7) will be free from ionic effects as was proved experimentally. Direct interaction between $S_2O_8^{2-}$ and M (equation 5) becomes possible now in spite of the α-methyl steric hindrance since electrostatic repulsion is absent here unlike in alkaline medium. Under similar conditions ($\mu = 1.2$ M; $t = 50°C$), the overall rate constant for polymerization in acid medium is higher (2.04 l mol^{-1} min^{-1}) than that in alkaline medium (3.05×10^{-2} l$^{1/2}$ mol$^{-1/2}$ min^{-1}).

Effect of pH on R_p

With increasing pH, methacrylic acid begins to dissociate into M^- and H^+. Hence the following reactions also become important.

$$M \underset{}{\overset{k_1}{\rightleftharpoons}} M^- + H^+ \qquad (9)$$

$$R_{n-1}^{\cdot} + M^- \xrightarrow{k_{p3}} R_n^{\cdot -} \qquad (10)$$

$$R_{n-1}^{\cdot} + M^- \xrightarrow{k_{p4}} R_n^{\cdot} \qquad (11)$$

$$R_n^{\cdot -} + R_m^{\cdot} \xrightarrow{k_{t3}} \text{Polymer} \qquad (12)$$

k_{p3} and k_{p4} may be expected to be almost equal to k_{p2} while k_{p1} will be much smaller because of electrostatic repulsion. Similarly k_{t2} and k_{t3} may be expected to be almost the same while k_{t1} will be much smaller. Hence, at least up to 50% dissociation, steps (5) to (12) will be the major reactions. Now variation in R_p with pH is caused mainly by the variation in the rate of initiation. Assuming $k_1 \ll k_3$, it can be easily deduced that R_p^2 depends upon $(1 - \alpha)$, where α is the degree of dissociation of methacrylic acid at a given pH. This was confirmed experimentally (*Figure 3*). This type of behaviour was also observed in the polymerization of acrylic acid with peroxodisulphate ion[4]. Pinner[5] has attributed the decrease in R_p of methacrylic acid with increasing pH, to the decrease in the rate of propagation, assuming a constant rate of initiation. Our results disprove his theory, at least up to 50% dissociation of the monomer. At higher pH, when

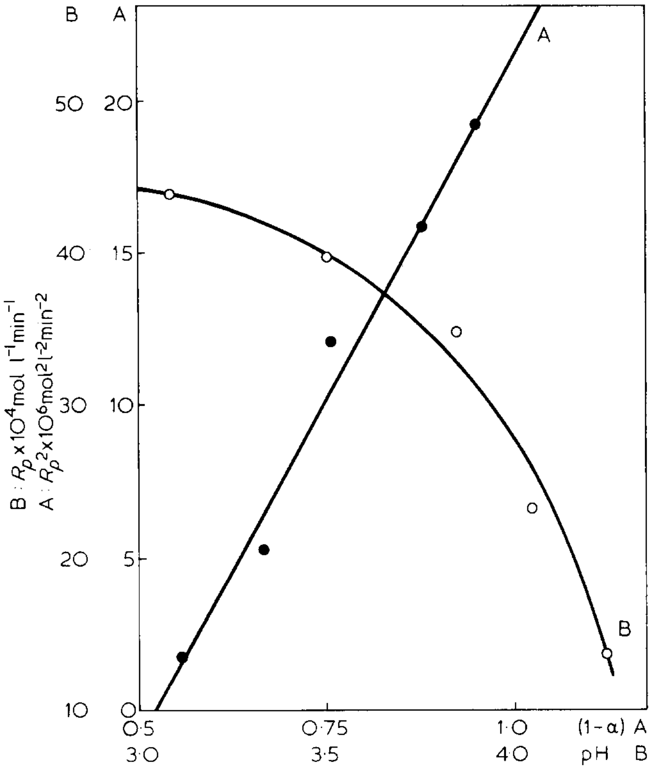

Figure 3 Dependence of R_p on pH in the polymerization of methacrylic acid and plot of R_p^2 *versus* $(1 - \alpha]$. $[M] = 0.1767$ mol.l^{-1}; $[S_2O_8^{2-}] = 0.01$ mol.l^{-1}, $\mu = 1.2$ mol.l^{-1}; $t = 35°C$

Table 1 Effect of Cu^2 on R_p when $[S_2O_8^{2-}$ = 0.02 M; [M] = 0.197 M; μ = 0.25 M; t = 35°C; $[H^+]$ = 0.1 M

$[Cu^{2+}] \times 10^4$ mole.l^{-1}	$R_p \times 10^4$ mole.l.$^{-1}$ min.$^{-1}$
0	49.30
1	46.96
20	35.76
100	21.86
400	19.40

$\alpha \geqslant 0.5$, reactions (1) to (4) also become important, making the kinetics complicated.

Ag^+ catalysis

A plot of log R_p versus log [M], log $[S_2O_8^{2-}]$ and log $[Ag^+]$ gave the values of slopes as 1.53, 0.24 and 0.25 respectively (*Figure 4*). Thus R_p depended very closely upon $[M]^{3/2}$, $[S_2O_8^{2-}]^{1/4}$ and $[Ag^+]^{1/4}$ in the presence of $AgClO_4$. When a plot of R_p versus $[Ag^+]^{1/4}$ is made a straight line passing through origin is obtained indicating that the contribution of the uncatalysed reaction was small. From the experiments at different temperatures, the enthalpy of activation for the Ag^+ catalysed reaction was calculated to be 5.8 kcal.mol^{-1} (*Figure 2*). The following mechanism was found to explain these results.

$$Ag^+(aq) + S_2O_8^{2-} \xrightleftharpoons{k_2} AgS_2O_8^-(aq) \tag{13}$$

$$AgS_2O_8^-(aq) \xrightarrow{k_5} Ag^+(aq) + HSO_4^- + \cdot OH + SO_4^{\cdot -} \tag{14}$$

$$Ag^+(Aq) + SO_4^{\cdot -} \xrightarrow{k_6} Ag^+(aq) + HSO_4^- + \cdot OH \tag{15}$$

$$\cdot OH + \cdot OH \xrightarrow{k_7} H_2O + O \tag{16}$$

$$\cdot OH + M \xrightarrow{k_8} R\cdot \tag{17}$$

$$R_{n-1}^{\cdot} + M \xrightarrow{k_{p2}} R_n^{\cdot} \tag{18}$$

$$R_n^{\cdot} + R_m^{\cdot} \xrightarrow{k_{t2}} \text{Polymer} \tag{19}$$

Under steady state conditions we get the relation,

$$R_p = \frac{k_{p2}k_8^{1/2}}{k_{t2}^{1/2}}\left(\frac{2k_5k_2}{k_7}\right)^{1/4}[M]^{3/2}[S_2O_8^{2-}]^{1/4}[Ag^+]^{1/4} \tag{20}$$

assuming that the reaction (equation 17) was much slower than reaction (equation 16). Equation (20) explains all our experimental results. Earlier studies[6] on the Ag^+ catalysed decomposition of $S_2O_8^{2-}$ showed that both $S_2O_8^{2-}$ and $SO_4^{\cdot -}$ are quickly converted to $\cdot OH$ in the presence of Ag^+(aq) and hence the initiation of polymerization by those two species becomes unimportant. Further, steric hindrance by the α-methyl group reduces the reactivity of the monomer and the $\cdot OH$ radicals disappear fast by the reaction (16). R_p in the presence of Ag^+ (aq) was found to be insensitive to variation of ionic strength. Complex species of the type AgM were found to be involved in the initiation step of the polymerization of acrylic acid[4] by $S_2O_8^{2-}$. Such species are obviously not involved in the case of methacrylic acid, which fact may again be attributed to the steric hindrance in the α-position of the monomer.

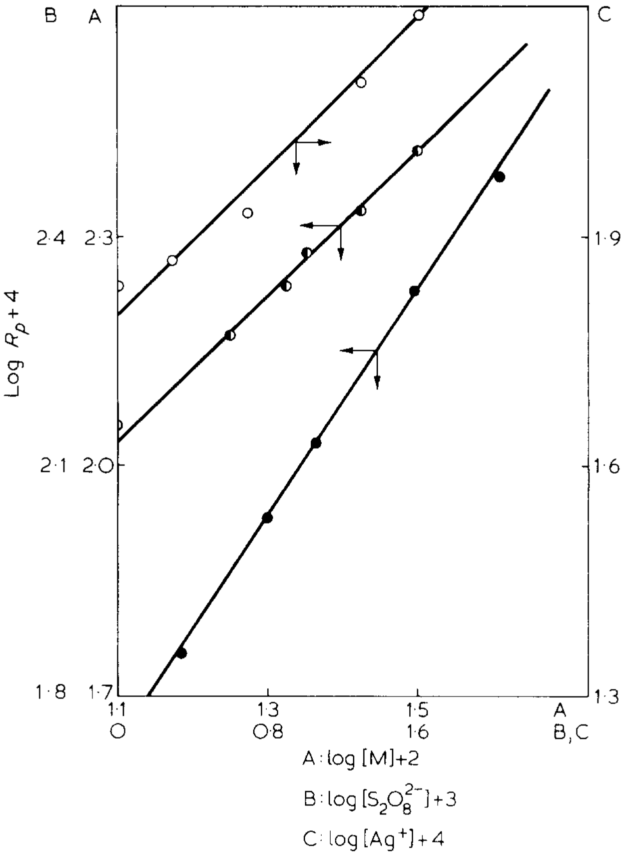

Figure 4 Plot of log R_p vs. log [M], log $[S_2O_8^{2-}]$ and log $[Ag^+]$ in the silver ion catalysed polymerization of methacrylic acid. log R_p vs. log[M]; slope = 1.53. Log R_p vs. log$[S_2O_8^{2-}]$; slope = 0.24. Log R_p vs. log$[Ag^+]$; slope = 0.25;. ●, $[S_2O_8^{2-}]$ = 0.91 mol.l^{-1}, $[Ag^+]$ = 2 x 10^{-4} mol.l^{-1}; ◑, [M] = 0.343 mol.l^{-1}; $[Ag^+]$ = 2 x 10^{-4} mol.l^{-1} ○, [M] = 0.128 mol.l^{-1}; $[S_2O_8^{2-}]$ = 0.01 mol.l^{-1}; μ = 0.22 mol.l^{-1}; $[H^+]$ = 0.1 mol.l^{-1}; t = 35°C

Effect of Cu^{2+} ions

At $[HClO_4]$ = 0.1 M, Cu^{2+} ions decreased the rate of polymerization of methacrylic acid by $S_2O_8^{2-}$ (*Table 1*), as was expected from our previous investigations[7]. The Cu^{2+} ions, acting as efficient radical traps, decrease R_p by terminating the polymer radicals.

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