Peroxo salts as initiators of vinyl polymerization: Polymerization of acrolein initiated by potassium peroxodiphosphate

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Kinetic studies were made on the polymerization of acrolein initated by potassium peroxodiphosphate (PP) in aqueous solution, in the presence and absence of Ag^+ ions. The rate of polymerization was found to depend on $[M]^{3/2}$ (M=monomer) and was independent of both [PP] and $[Ag^+]$. The overall activation energy was calculated to be 4.8 kcal mol^{-1}. A mechanism involving termination by PO_4^{2-} radicals is proposed and discussed.

Keywords Kinetics; polymerization; peroxodiphosphate; acrolein; phosphate radicals; silver ion catalysis

INTRODUCTION

Previous reports indicate that the most conventional method of preparation of polyacrolein is through suspension polymerization[1-3] of the monomer initiated by a persulphate–silver ion system in water. Recently peroxodiphosphate ion was successfully used by us as an initiator for the polymerization of acrylamide[4] and methacrylic acid[5] with or without catalysis by Ag^+ ions. As a continuation of these investigations, we have studied the kinetics of the polymerization of acrolein (ACR) initiated by peroxodiphosphate (PP) in a neutral medium.

EXPERIMENTAL

Acrolein (Riedel) stabilized with hydroquinone was distilled before use under nitrogen[6]. A few strings of copper wire were added to the monomer during distillation to prevent any slight fogging due to spontaneous polymerization. Potassium peroxodiphosphate (F.M.C. Corporation, USA) was twice recrystallized from methanol[7]. $AgNO_3$ (BDH,AR) and Na_2SO_4 (BDH,AR) (to maintain the ionic strength of the medium) were used without further purification. Water, double-distilled over alkaline permanganate and deionized by passing through Biodeminrolit resin (Permutit Co., UK), was used to prepare the reagents. The reaction mixture was deaerated by passing oxygen-free nitrogen over the mixture and the temperature was controlled to within ±0.01°C. The rate of polymerization, R_p, was measured by estimating the monomer concentration at various time intervals by bromometry[8]. Reaction mixtures containing $AgNO_3$ were excluded from daylight.

RESULTS AND DISCUSSION

The rate of polymerization was found to be dependent on $[M]^{3/2}$ and $[PP]^0$ under the conditions:

$$[PP]=0.004\text{–}0.01\ mol\,l^{-1},\ [Ag^+]=0\text{–}1.0\times10^{-3}\ mol\,l^{-1},\ \mu=0.1\ mol\,l^{-1}$$
$$\text{and temperature}=50°C.$$

However, when the experiments were repeated, in the presence of Ag^+ ions, the rate was found to be independent of both $[Ag^+]$ and [PP] (*Table 1*) and therefore dependent only on $[M]^{3/2}$ (*Figure 1*). Thus, polymerization of acrolein initiated by peroxodiphosphate proved to be unique in that, the concentration of Ag^+ ions has no effect on the rate of the reaction. The overall activation energy for the polymerization was calculated to be 4.9 kcal mol^{-1} from the Arrhenius plot (*Figure 1*). The rate of polymerization was also found to be insensitive to a change in the ionic strength of the medium.

The following mechanism will explain all these observations. $HP_2O_8{}^{3-}$ was assumed to be the major species present in neutral medium[9], from a knowledge of the population of different species of peroxodiphosphate as a function of pH.

$$HP_2O_8{}^{3-}\xrightarrow{k_1}2PO_4{}^{\cdot 2-}+H^+ \qquad (1)$$

$$PO_4{}^{\cdot 2-}+M\xrightarrow{k_2}M_1^{\cdot} \qquad (2)$$

$$M_n^{\cdot}+M\xrightarrow{k_p}M_n^{\cdot}+1 \qquad (3)$$

$$M_n^{\cdot}+HP_2O_8{}^{3-}\xrightarrow{k_3}P_n+PO_4{}^{\cdot 2-}+H^+ \qquad (4)$$

$$M_n^{\cdot}+PO_4^{\cdot 2-}\xrightarrow{k_{t_1}}P_n \qquad (5)$$

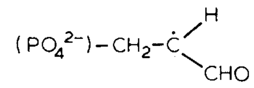
where $M_1^{\cdot}$ and P_n denote  $(PO_4^{2-})\text{–}CH_2\text{–}\dot{C}(H)(CHO)$ and a

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Table 1 Effect of [PP] and [Ag^+] on the rate of polymerization of Acrolein initiated by potassium peroxodiphosphate. Temperature = 50° C; μ = 0.1 mol. l^{-1}. [Ag^+] = 0; [Ag^+] = 10^{-3} mol. l^{-1} [PP] = 0.01 mol. l^{-1} [M] = 0.243 mol. l^{-1}; [M] = 0.146 mol. l^{-1} [M] = 0.151 mol. l^{-1}

[PP] mol. l^{-1}	$R_p \times 10^5$ mol. l^{-1} s^{-1}	$R_p \times 10^5$ mol. l^{-1} s^{-1}	$Ag^+ \times 10^3$ mol. l^{-1}	$R_p \times 10^5$ mol. l^{-1} s^{-1}
0.002	3.77	1.76	1.0	2.10
0.004	3.29	1.63	1.5	2.19
0.006	3.48	1.95	2.0	2.10
0.008	3.68	1.85	2.5	2.10
0.010	3.58	2.04	3.0	2.10

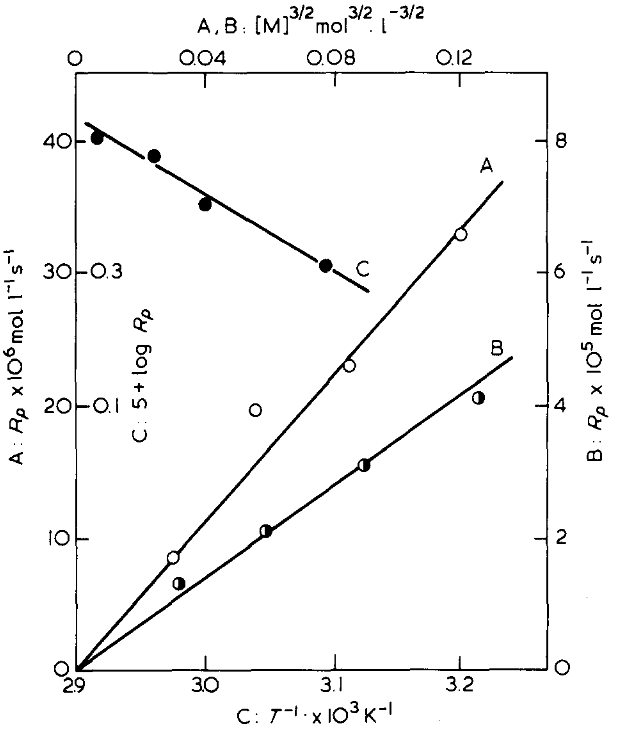


Figure 1 Polymerization of acrolein initiated by potassium peroxodiphosphate. A: R_p vs. $[M]^{3/2}$; [PP] = 0.004 mol. l^{-1}; [Ag^+] = 0; μ = 0.1 mol. l^{-1}; t = 50°C. B: R_p vs. $[M]^{3/2}$; [PP] = 0.01 mol. l^{-1}; [Ag^+] = 1.0×10^{-3} mol. l^{-1}; μ = 0.1 mol. l^{-1}; t = 50°C. C: log R_p vs. $1/T$; [PP] = 0.01 mol. l^{-1}; [M] = 0.146 mol. l^{-1}; μ = 0.1 mol. l^{-1}

polymer molecule with chain length '*n*' respectively. Under steady state conditions,

$$R_p = \frac{k_p}{k_{t_1}^{\frac{1}{2}}}\left(\frac{k_1 k_2}{k_3}\right)^{\frac{1}{2}}[M]^{3/2} \tag{6}$$

The experimental results were found to agree well with the rate expression derived. The non-dependence of the rate of polymerization on [PP] indicated that the growing radicals are terminated by PP and the primary radicals, $PO_4^{\cdot 2-}$. The dependence of rate on $[M]^{3/2}$ necessitates the assumption $k_3 k_{t_1}[M_n^{\cdot}]^2 \gg k_1 k_{t_1}[M_n^{\cdot}]$ which is unusual. This incidentally confirms the preponderence of fast chain transfer to the initiator as compared with the slow decomposition of $HP_2O_8{}^{3-}$. It was also evident that acrolein is not very reactive towards polymerization by PP, from the rate constant, $\frac{k_p}{k_{t_1}^{\frac{1}{2}}}\left(\frac{k_1 k_2}{k_3}\right)^{\frac{1}{2}}$, which was calculated to be 2.80×10^{-4} $mol^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$ s^{-1} at 50°C.

In the presence of $AgNO_3$, a new set of reactions occurs.

$$2Ag^+ + HP_2O_8{}^{3-} \overset{K}{=\!=} Ag_2HP_2O_8{}^- \tag{7}$$

$$Ag_2HP_2O_8{}^- + H_2O \xrightarrow{k_4} Ag_2HPO_4 + HPO_4^{\cdot -} + \dot{O}H \tag{8}$$

$$Ag^+ + HPO_4^{\cdot -} + H_2O \xrightarrow{k_5} AgH_2PO_4 + \dot{O}H \tag{9}$$

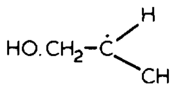
$$Ag_2HP_2O_8{}^- + M + H_2O \xrightarrow{k_6} M_1^{\cdot} + Ag_2HPO_4 + HPO_4^{\cdot -} \tag{10}$$

$$\dot{O}H + M \xrightarrow{k_7} M_1^{\cdot} \tag{11}$$

$$M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot} \tag{12}$$

$$M_n^{\cdot} + Ag_2HP_2O_8{}^- + H_2O \xrightarrow{k_8} P_n + HPO_4^{\cdot -} + Ag_2HPO_4 \tag{13}$$

$$M_n^{\cdot} + \dot{O}H \xrightarrow{k_{t_2}} P_n \tag{14}$$

where $M_1^{\cdot}$ represents the species  $HO.CH_2{-}\dot{C}(H)CHO$ and P_n is a hydroxyl terminated polymer. Under steady state conditions and assuming $k_8 k_{t_2}[M_n^{\cdot}]^2 \gg k_4 k_{t_2}[M_n^{\cdot}]$, we can derive an expression for the rate of polymerization, i.e.,

$$R_p = \frac{k_p}{k_{t_2}^{\frac{1}{2}}}\left(\frac{k_4 k_7}{k_8}\right)^{\frac{1}{2}}[M]^{3/2} \tag{15}$$

This rate expression is in good agreement with the experimental result, i.e., the rate depends only on $[M]^{3/2}$.

The formation of a complex of Ag^+ with PP in neutral medium was reported earlier[10]. The absence of a salt effect supports the mechanism proposed since [$Ag_2HP_2O_8{}^-$] is absent in the rate equation. The polymer radicals are terminated by both $Ag_2HP_2O_8^-$ and .OH radicals. The composite rate constant $\frac{k_p}{k_{t_2}^{\frac{1}{2}}}\left(\frac{k_4k_7}{k_8}\right)^{\frac{1}{2}}$ was calculated to be 3.46×10^{-4} mol$^{-\frac{1}{2}}$ l$^{\frac{1}{2}}$ s^{-1} ([Ag^+]$=1.0\times10^{-3}$ mol l^{-1}; 50°C) and it was surprisingly close to a similar value for the uncatalysed system. The non-involvement of the monomer molecule in the radical producing processes (step 8) clearly indicates that the rate of its reaction with $Ag_2HP_2O_8^-$ (step 10) was much lower than the rate of decomposition of $Ag_2HP_2O_8^-$ (step 8).

Chain transfer by $HP_2O_8^-$ in an uncatalysed system and by $Ag_2HP_2O_8^-$ in the catalysed system were also included to explain the experimental results. However, termination of polymerization by PO_4^{2-} and ·OH in the uncatalysed and Ag^+-catalysed system respectively were encountered for the first time in this system. Similar termination and chain transfer by the initiating complex species were reported earlier in the polymerization of other vinyl monomers.

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