Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Manickam, S. P. , Subbaratnam, N. R. and Venkatarao, K.(1981) 'Peroxo Salts as Initiators of Vinyl Polymerization. 6. Kinetics of Polymerization of Acrylonitrile Initiated by Potassium Peroxodisulfate in Aqueous Medium-Ag Catalysis', Journal of Macromolecular Science, Part A, 15: 8, 1511 — 1519

To link to this Article: DOI: 10.1080/00222338108056798

URL: http://dx.doi.org/10.1080/00222338108056798

J. MACROMOL. SCI.–CHEM., A15(8), pp. 1511-1519 (1981)

Peroxo Salts as Initiators of Vinyl Polymerization. 6. Kinetics of Polymerization of Acrylonitrile Initiated by Potassium Peroxodisulfate in Aqueous Medium-Ag^+ Catalysis

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ABSTRACT

The kinetics of polymerization of acrylonitrile initiated by potassium peroxodisulfate in neutral and acid conditions was studied. R_p depended upon $[S_2O_8^{2-}]^{1/2}$ and $[\text{monomer}]^{3/2}$ both in neutral and acid solutions. The influence of ionic strength and the catalytic effect of Ag^+ on the system are discussed. Suitable mechanisms are proposed.

INTRODUCTION

Studies on the kinetics of polymerization of acrylonitrile in aqueous medium initiated by peroxodisulfate by different workers [1-3] gave conflicting results. In order to get a clear picture of the kinetics and also as a continuation of our earlier studies [4-9] on peroxodisulfate-initiated vinyl polymerization, we made a reinvestigation of the polymerization of acrylonitrile in water, both in acid and neutral conditions. For the first time, the effect of Ag^+ ions on this system was also looked into. The kinetic results of our investigations and the mechanisms proposed are presented here.

EXPERIMENTAL

Acrylonitrile (E. Merck, G.R.) was purified by double distillation under reduced pressure after washing with sodium hydroxide solution followed by water [10]. Potassium peroxodisulfate (E. Merck, G.R.) was twice recrystallized from double distilled water. $AgClO_4$ and $NaClO_4$ were prepared as described in our earlier papers [4, 5]. Water, distilled over alkaline permanganate, was used for the preparation of reagents. The reaction mixtures were always flushed with oxygen-free nitrogen. The temperature of the reaction mixture was controlled to ±0.01°C in a thermostat. The rate of polymerization, R_p, was evaluated gravimetrically and the molecular weight of the polymer determined by viscometry using the Mark-Houwink equation, $[\eta] = 24.3 \times 10^{-3} \times M^{0.75}$ at 25°C in dimethylformamide [11]. The molecular weights of the polymers were estimated to be in the range $19\text{-}36 \times 10^4$.

RESULTS AND DISCUSSION

Uncatalyzed Polymerization in Neutral and Acid Media

With $[M] = 0.48\text{-}1.08$ mol/L and $[S_2O_8{}^{2-}] = 0.002\text{-}0.032$ mol/L, R_p was found to depend on $[M]^{3/2}$ and $[S_2O_8{}^{2-}]^{1/2}$ in neutral medium. Plots of R_p versus $[M]^{3/2}$ (Fig. 1) and $[S_2O_8{}^{2-}]^{1/2}$ (Fig. 2) were linear, passing through the origin. With constant $[S_2O_8{}^{2-}]$, $[M]$, and temperature, R_p decreased slightly with increasing ionic strength of the media (Table 1). From the experiments at different temperatures, the overall activation energy for the polymerization in neutral medium was computed to be 17.7 kcal/mol (Fig. 3). The kinetic experiments were repeated in acid medium with $[HClO_4] = 1.0$ mol/L. The

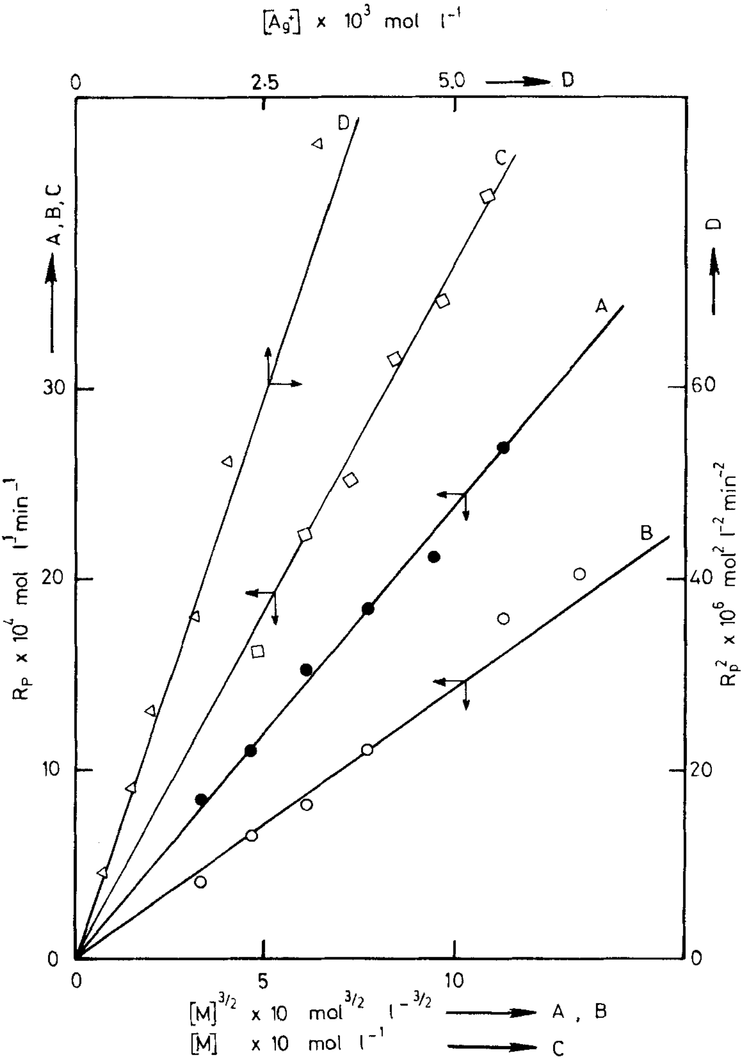

FIG. 1. Dependence of R_p on $[M]^{3/2}$ in neutral and acid media: R_p vs $[M]^{3/2}$, $[S_2O_8^{2-}] = 0.01$ mol/L, t = 50°C (A, $\mu = 0.12$ mol/L; B, $\mu = 1.12$ mol/L; $[H^+] = 1.0$ mol/L. Dependence of R_p on [M] in the Ag^+ catalyzed system and the effect of Ag^+ on R_p: $[S_2O_8^{2-}] =$ 0.01 mol/L, $\mu = 0.12$ mol/L, t = 35°C (R_p vs [M]; C, $[Ag^+] = 4 \times 10^{-4}$ mol/L; R_p^2 vs $[Ag^+]$; D, [M] = 0.84 mol/L).

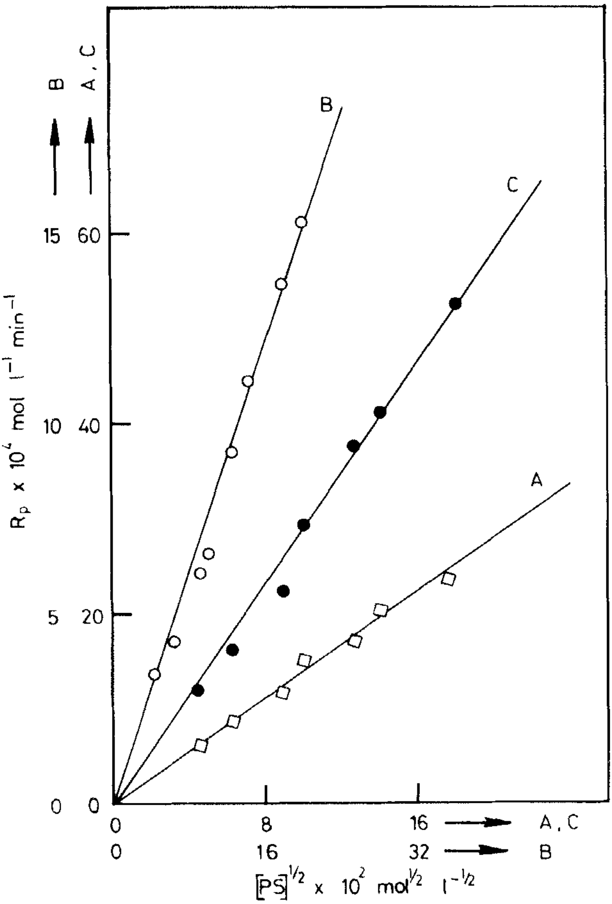

FIG. 2. Dependence of R_p on $[S_2O_8^{2-}]^{1/2}$ in neutral and acid media and in the Ag^+ catalyzed system. R_p vs $[S_2O_8^{2-}]^{1/2}$, t = 50°C (A, [M] = 0.72 mol/L, μ = 0.12 mol/L; B, [M] = 0.6 mol/L, $[H^+]$ = 1.0 mol/L, μ = 1.12 mol/L); C, [M] = 0.84 mol/L, $[Ag^+]$ = 4×10^{-4} mol/L, μ = 0.12 mol/L, t = 35°C.

TABLE 1. Effect of Ionic Strength on the Rate of Polymerization of Acrylonitrile

t (°C)	[M] (mol/L)	$[S_2O_8^{2-}]$ (mol/L)	$[H^+]$ (mol/L)	$[Ag^+] \times 10^4$ (mol/L)	μ (mol/L)	$R_p \times 10^4$ (mol/L min)
50	0.84	0.02	1.0	-	1.12	18.8
50	0.84	0.02	1.0	-	1.50	18.4
50	0.84	0.02	1.0	-	1.70	18.6
50	0.84	0.02	1.0	-	1.90	18.1
50	0.84	0.02	1.0	-	2.10	18.5
50	0.72	0.01	-	-	0.3	22.4
50	0.72	0.01	-	-	0.5	20.8
50	0.72	0.01	-	-	0.7	15.5
50	0.72	0.01	-	-	0.9	15.2
35	0.84	0.01	-	4.0	0.12	31.5
35	0.84	0.01	-	4.0	0.32	30.8
35	0.84	0.01	-	4.0	0.52	29.7
35	0.84	0.01	-	4.0	0.72	28.2
35	0.84	0.01	-	4.0	0.92	27.6

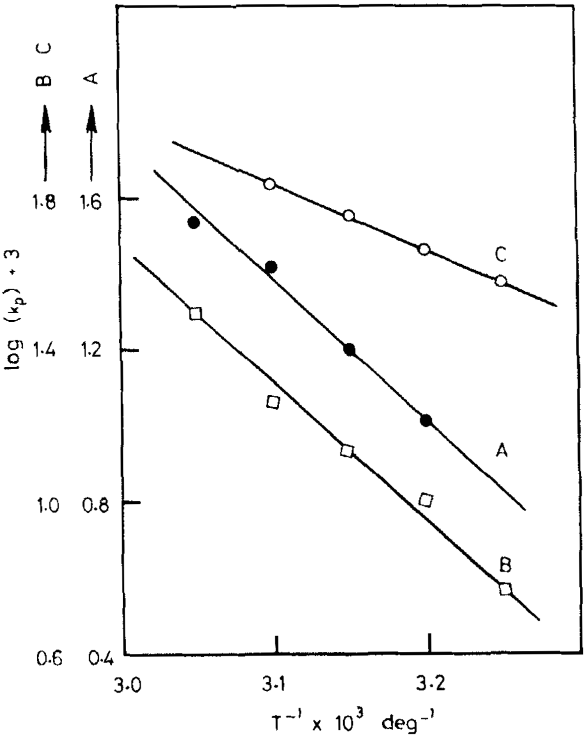

FIG. 3. Plot of log k vs T^{-1} for the polymerization of acrylonitrile in neutral and acid media and in the Ag^+ catalyzed system. $[S_2O_8^{2-}] = 0.01$ mol/L, $\mu = 0.12$ mol/L (A, $[M] = 1.08$ mol/L; C, $[M] = 0.84$ mol/L, $[Ag^+] = 4 \times 10^{-4}$ mol/L); B, $[M] = 1.2$ mol/L, $[H^+] = 1.0$ mol/L, $[S_2O_8^{2-}] = 0.02$ mol/L, $\mu = 1.12$ mol/L.

reactions were found to follow the same rate law as in neutral medium (Figs. 1 and 2), and R_p was found to be insensitive to changes in ionic strength of the medium (Table 1). The activation energy was found to be slightly lower (16.6 kcal/mol) (Fig. 3). The following mechanism explains our kinetic results in both neutral and acid conditions.

$$S_2O_8^{2-} + M \xrightarrow{k_0} R\cdot + SO_4^{\cdot -} \tag{1}$$

$$SO_4^{\cdot -} + M \xrightarrow{k_1} R^{\cdot} \tag{2}$$

$$R_n^{\cdot} + M \xrightarrow{k_p} R^{\cdot}_{(n+1)} \tag{3}$$

$$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_t} \text{polymer} \tag{4}$$

where $R^{\bullet}$ represents the primary ion-radical $^{-}O_4S\text{–}CH_2\text{–}\dot{C}H\text{–}CN$. Under steady-state conditions, assuming unit initiator efficiency,

$$R_p = \frac{\sqrt{2}k_p k_0^{1/2}}{k_t^{1/2}} [S_2O_8^{2-}]^{1/2} [M]^{3/2} \tag{5}$$

which agrees well with our experimental data. The slight decrease in R_p with increasing ionic strength in neutral medium may be explained as an effect on the ion-dipole reaction in Step (1). But in acid medium, $S_2O_8^{2-}$ may be protonated to become $HS_2O_8^{-}$. Now the effect of ionic strength on the reaction is less pronounced since the charge on the ion has decreased. Further, at such high ionic strengths (μ = 1.2 mol/L) used in acid medium, ion-pair formation involving both $S_2O_8^{2-}$ and monomer may decrease the effective charge on these species, thereby minimizing the magnitude of the ionic strength effect. Formation of the primary radical ions $^{-}O_4S\text{–}CH_2\text{–}\dot{C}H\text{–}CN$ was proposed since Ledwith and Russell [12] have pointed out that the electron transfer from olefins carrying electron-withdrawing group to $SO_4^{\bullet -}$ (or $S_2O_8^{2-}$) is highly improbable due to energy considerations. Hence acrylonitrile either gives a polymer with SO_4 end groups by direct interaction with $S_2O_8^{2-}$ and $SO_4^{\bullet -}$ or with OH end groups when $SO_4^{\bullet -}$ radical ions escape from the monomer, and give $^{\bullet}OH$ radicals by interacting with water [13, 14]. Trubitsyna et al. [3] suggested the formation of monomer-peroxodisulfate complexes which decompose to yield initiating radicals. Spectral studies by us did not reveal any conclusive evidence for the formation of complexes. Tsuruta et al. [1] reported the dependence of R_p on $[S_2O_8^{2-}]$ which was not in agreement with our results. R_p was found to depend on $[S_2O_8^{2-}]^{1/2}$ and, under our experimental conditions, there was no evidence for unimolecular initiation.

Ag^+ Catalyzed Polymerization in Neutral Medium

In the presence of $AgClO_4$ in neutral medium, R_p depended on $[S_2O_8^{2-}]^{1/2}$, $[Ag^+]^{1/2}$, and $[M]$. Plots of R_p versus $[M]$ (Fig. 1) and $[S_2O_8^{2-}]^{1/2}$ (Fig. 2) were linear, passing through the origin. The plot of R_p^2 versus $[Ag^+]$ (Fig. 1) was also linear, passing through the origin, indicating that there is no contribution of uncatalyzed polymerization to R_p under the experimental conditions. From a plot of log k against T^{-1} (Fig. 3), the overall activation energy for the catalyzed polymerization was calculated to be 8 kcal/mol with $[Ag^+] = 4.0 \times 10^{-4}$ mol/L. R_p decreased slightly with increasing ionic strength of the medium (Table 1). The following reactions, in addition to the reactions given earlier (Eqs. 1-4), will explain the Ag^+ catalyzed polymerization.

$$Ag^+(aq) + S_2O_8^{2-} \overset{K}{\rightleftharpoons} AgS_2O_8^-(aq) \tag{6}$$

$$AgS_2O_8^-(aq) \xrightarrow{k_2} Ag^+(aq) + HSO_4^- + SO_4^{\bullet -} + {}^\bullet OH \tag{7}$$

$$Ag^+(aq) + SO_4^{\bullet -} \xrightarrow{k_3} Ag^+(aq) + HSO_4^- + {}^\bullet OH \tag{8}$$

$${}^\bullet OH + M \xrightarrow{k_4} R^\bullet \tag{9}$$

Assuming steady-state conditions and independence of k_p and k_t on chain length, we get

$$R_p = \frac{\sqrt{2}k_p}{k_t^{1/2}} (k_0 + k_2K[Ag^+])^{1/2}[S_2O_8^{2-}]^{1/2}[M] \tag{10}$$

where $(1 + K[Ag^+]) \approx 1$. This expression confirms the absence of direct interaction between monomer and $AgS_2O_8^-(aq)$, which agrees well with our experimental results. The slight negative salt-effect agrees with the involvement of Equilibrium (6) in the reaction sequence. Formation of the reactive ion pair $AgS_2O_8^-(aq)$ was proposed on the basis of our earlier studies [7]. The presence of the –CN group in the monomer decreases the π-electron density, thereby making its reaction with $S_2O_8^{2-}$ or $SO_4^{\bullet -}$ less favorable in general. But in the case of uncatalyzed polymerization, this reaction between monomer and $S_2O_8^{2-}$ is still fast as compared to the homolysis of $S_2O_8^{2-}$, and in the Ag^+ catalyzed system the decomposition of $AgS_2O_8^-(aq)$ is fast as compared to its reaction with the monomer. As a result, the monomer exponent is reduced to unity. The absence of direct interaction between $AgS_2O_8^-(aq)$ and monomer may be attributed to the inactive nature of the monomer itself, brought about by the presence of the electron-withdrawing –CN group.

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Accepted by editor December 27, 1979
Received for publication March 5, 1980