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## 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** Hussain, S. Anwar , Tajuddin, I. and Anwaruddin, Q.(1984) 'Polymerization of Acrylonitrile Initiated by the Redox System Peroxydisulfate-Cyclohexanol in the Presence of Silver Ion Catalyst', Journal of Macromolecular Science, Part A, 21: 2, 215 – 224

**To link to this Article:** DOI: 10.1080/00222338408056550

**URL:** <http://dx.doi.org/10.1080/00222338408056550>

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## **Polymerization of Acrylonitrile Initiated by the Redox System Peroxydisulfate-Cyclohexanol in the Presence of Silver Ion Catalyst**

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### **ABSTRACT**

The kinetics of the polymerization of acrylonitrile initiated by the redox system peroxydisulfate-cyclohexanol catalyzed by silver ion has been studied. The rate of polymerization was found to be directly proportional to the first power of monomer concentration and the square roots of peroxydisulfate, cyclohexanol, and silver ion concentrations. The effect of temperature has been investigated in the range of 35 to 60°C and the overall activation energy was found to be 4.6 kcal/mol from the Arrhenius plot. A plausible kinetic scheme has been proposed to account for the observations.

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## INTRODUCTION

Silver ion was used as a catalyst in the oxidation of alcohols by peroxydisulfate [1-4]. Silver ion also found use as a catalyst in the redox system initiated thermal polymerization of vinyl monomers [5, 6]. Kagiya et al. [7] have reported the polymerization of acrolein by the peroxydisulfate-silver nitrate redox system, whereas Manickam et al. used the same initiator system for the polymerization of methacrylic acid [8], acrylic acid [9], acrylamide [10], methacrylamide [11], and acrylonitrile [12]. Quantitative determination of the aldehyde group was made in the case of acrolein [7], and the polymerization was classified as a nonstationary state. Nayak and co-workers have polymerized acrylonitrile [13] and methyl methacrylate [14] using the peroxydisulfate-citric acid redox system catalyzed by silver ion. Hydroxyl endgroups were reported to be absent. In the present paper we report the polymerization of acrylonitrile initiated by the redox system potassium peroxydisulfate-cyclohexanol in the presence of silver ion catalyst.

## EXPERIMENTAL

Acrylonitrile was purified by successively washing with 5% NaOH, 3% orthophosphoric acid, and water, then dried over anhydrous calcium chloride, and distilled. Cyclohexanol (E. Merck sample) was distilled before use. All other reagents used were AnalaR grade. Distilled water was further purified by a second distillation over alkaline permanganate and used for preparing all the solutions.

Required quantities of the monomer, cyclohexanol, and silver nitrate were introduced in a reaction vessel which was then thermostated. Polymerization was initiated by adding freshly prepared solutions of peroxydisulfate. Zero time of the reaction corresponded to the complete addition of peroxydisulfate. To arrest the polymerization reaction after the intended period of time, 1% hydroquinone solution in 2 N H<sub>2</sub>SO<sub>4</sub> was added and the precipitated polymer was filtered.

## RESULTS AND DISCUSSION

Effect of Monomer Concentration

The nonstationary steady-state was attained in 70 min for the polymerization reaction and the same reaction time was maintained in all our experiments. A small induction period was observed and it was neglected. Figure 1 illustrates the dependence of the rate of polymerization on the monomer concentration. The order with respect to monomer was unity. The concentration of monomer was varied over the range 15.17

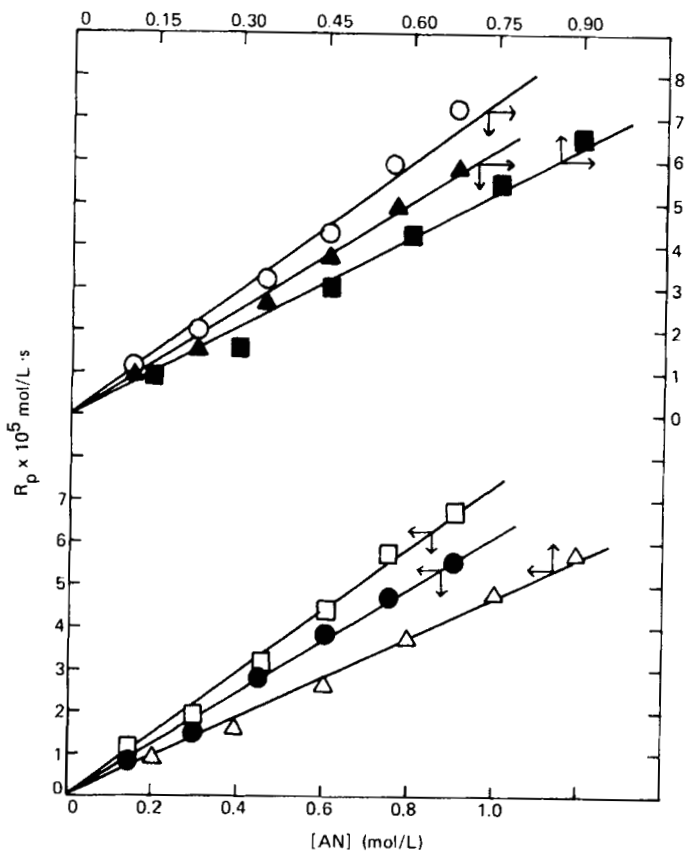


FIG. 1. Plot of  $R_p$  vs  $[\text{AN}]$  at  $40^\circ\text{C}$ :  $[\text{Cyclohexanol}] = 4.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-3} \text{ M}$ , (●)  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-3} \text{ M}$ , (▲)  $[\text{S}_2\text{O}_8^{2-}] = 1.0 \times 10^{-2} \text{ M}$ , (△)  $[\text{S}_2\text{O}_8^{2-}] = 1.5 \times 10^{-2} \text{ M}$ .  $R_p$  vs  $[\text{AN}]$  at  $50^\circ\text{C}$ :  $[\text{Cyclohexanol}] = 4.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-3} \text{ M}$ , (■)  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-3} \text{ M}$ , (□)  $[\text{S}_2\text{O}_8^{2-}] = 1.0 \times 10^{-2} \text{ M}$ , (○)  $[\text{S}_2\text{O}_8^{2-}] = 1.5 \times 10^{-2} \text{ M}$ .

to  $91.03 \times 10^{-2}$  M at 40 and 50°C and at three different concentrations of peroxydisulfate:  $5.0 \times 10^{-3}$ ,  $1.0 \times 10^{-2}$ , and  $1.5 \times 10^{-2}$  M. A first-order dependence of rate on monomer concentration implies that the monomer is not involved in the radical production step.

### Effect of Peroxydisulfate Concentration

The rate of polymerization was investigated by varying the concentration of peroxydisulfate in the range  $2.0 \times 10^{-3}$  to  $1.4 \times 10^{-2}$  M at monomer concentrations of  $30.34 \times 10^{-2}$ ,  $60.68 \times 10^{-2}$ , and  $91.03 \times 10^{-2}$  M at two different temperatures, 40 and 50°C. Plots of  $R_p$  vs  $[S_2O_8^{2-}]^{1/2}$  (Fig. 2) are linear, showing a square root dependence on peroxydisulfate. Since either cyclohexanol or silver nitrate alone is incapable of initiating polymerization under our reaction conditions, the reactive species should result from the interactions of peroxydisulfate,  $Ag^+$ , and cyclohexanol. According to generally accepted kinetic principles, an exponent of 0.5 leads to mutual termination of radicals, as established in a number of cases. Manickam et al. [12] and Nayak et al. [13, 14] reported similar results involving peroxydisulfate as oxidant.

### Effect of Cyclohexanol Concentration

Increasing the cyclohexanol concentration results in a linear increase in the rate of polymerization. Order with respect to cyclohexanol is 0.5 (Fig. 3). The concentration of cyclohexanol was varied between 1.0 and  $6.0 \times 10^{-2}$  M at 40 and 50°C and at three different concentrations of peroxydisulfate.

### Effect of Silver Ion Concentration

The rate of polymerization was proportional to  $[Ag^+]^{1/2}$  (Fig. 4). Keeping all the other variables unchanged, the concentration of silver ion was varied over the range  $3.0 \times 10^{-4}$  to  $2.0 \times 10^{-3}$  M. The rate increases linearly with increasing silver ion concentration. A similar order was reported by Riggs and co-workers [15] for the polymerization of acrylamide initiated by peroxydisulfate.

### Effect of Temperature

The effect of temperature on the rate of polymerization is shown in Fig. 5. The temperature was varied within from 35 to 60°C. From the slope of the Arrhenius plot of  $\log R_p$  vs  $1/T$ , the overall activation

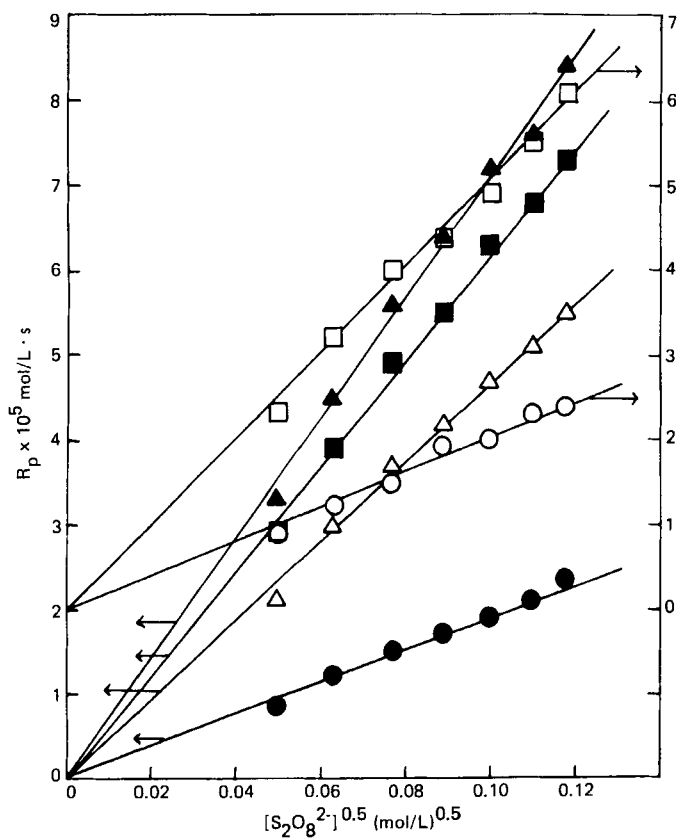


FIG. 2. Plot of  $R_p$  vs  $[S_2O_8^{2-}]^{1/2}$  at  $40^\circ\text{C}$ :  $[\text{Cyclohexanol}] = 4.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-3} \text{ M}$ , (●)  $[\text{AN}] = 0.3034 \text{ M}$ , (Δ)  $[\text{AN}] = 0.6068 \text{ M}$ , (◻)  $[\text{AN}] = 0.6068 \text{ M}$ , (◼)  $[\text{AN}] = 0.9103 \text{ M}$ .  $R_p$  vs  $[S_2O_8^{2-}]^{1/2}$  at  $50^\circ\text{C}$ :  $[\text{Cyclohexanol}] = 4.0 \times 10^{-2} \text{ M}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-3} \text{ M}$ , (○)  $[\text{AN}] = 0.3034 \text{ M}$ , (◻)  $[\text{AN}] = 0.6068 \text{ M}$ , (▲)  $[\text{AN}] = 0.9103 \text{ M}$ .

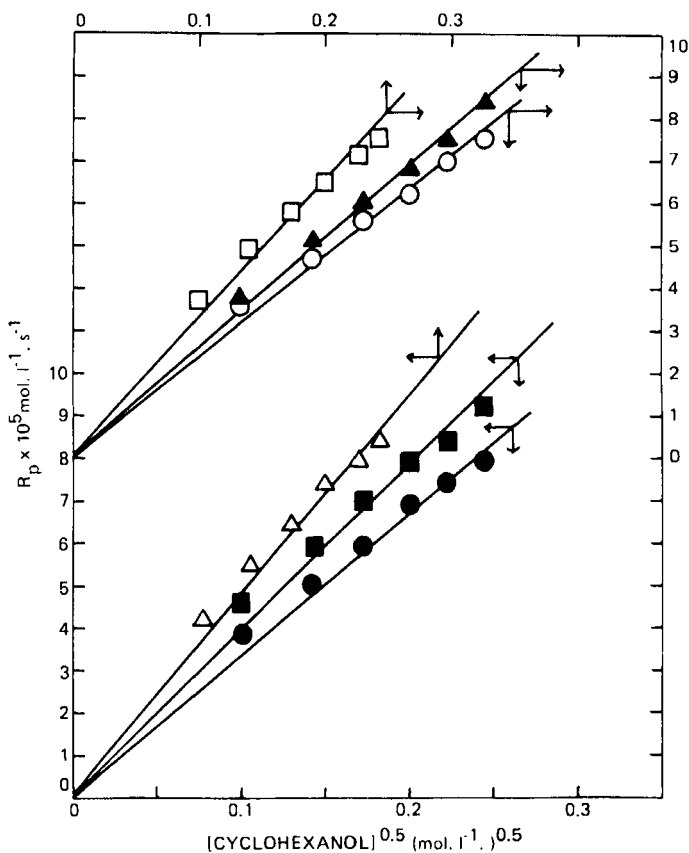


FIG. 3. Plot of  $R_p$  vs  $[\text{cyclohexanol}]^{1/2}$  at 40°C:  $[\text{AN}] = 0.9103 \text{ M}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-3} \text{ M}$ , ( $\circ$ )  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-3} \text{ M}$ , ( $\square$ )  $[\text{S}_2\text{O}_8^{2-}] = 1.0 \times 10^{-2} \text{ M}$ , ( $\blacktriangle$ )  $[\text{S}_2\text{O}_8^{2-}] = 1.5 \times 10^{-2} \text{ M}$ .  $R_p$  vs  $[\text{cyclohexanol}]^{1/2}$  at 50°C:  $[\text{AN}] = 0.9103 \text{ M}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-3} \text{ M}$ , ( $\bullet$ )  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-3} \text{ M}$ , ( $\triangle$ )  $[\text{S}_2\text{O}_8^{2-}] = 1.0 \times 10^{-2} \text{ M}$ , ( $\blacksquare$ )  $[\text{S}_2\text{O}_8^{2-}] = 1.5 \times 10^{-2} \text{ M}$ .

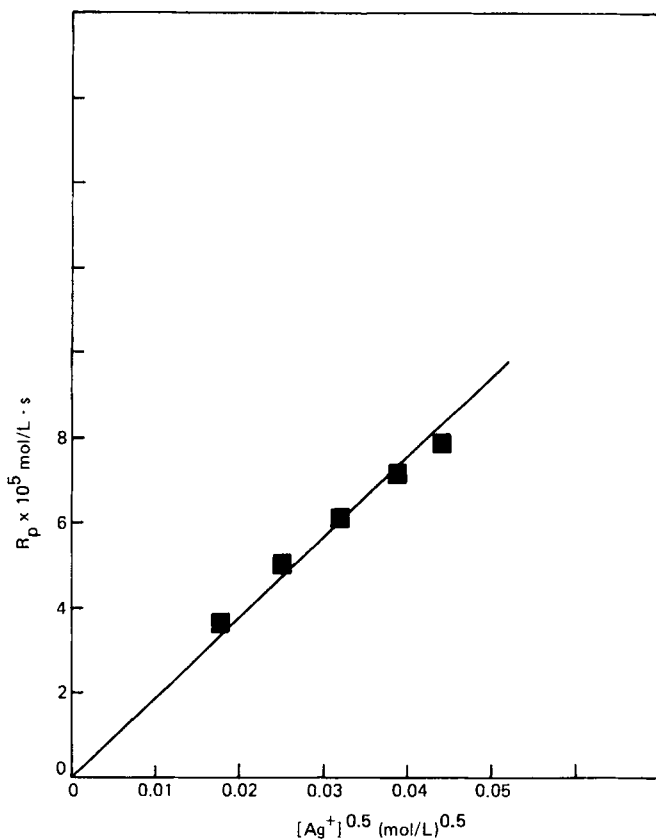


FIG. 4. Plot of  $R_p$  vs  $[Ag^+]^{1/2}$  at  $50^\circ C$ :  $[AN] = 0.9103 \text{ M}$ ,  $[S_2O_8^{2-}] = 1.0 \times 10^{-2} \text{ M}$ ,  $[\text{cyclohexanol}] = 4.0 \times 10^{-2} \text{ M}$ .

energy was calculated to be 4.6 kcal/mol. Nayak et al. [13] have reported an activation energy closer to this value for the polymerization of acrylonitrile initiated by the redox system peroxydisulfate-citric acid- $Ag^+$  ion.

#### Effect of Organic Solvents

The presence of small amounts (4% v/v) of certain water-miscible organic solvents like methanol, ethanol, and acetone tends to depress the initial rate of polymerization. Such effects have been reported in



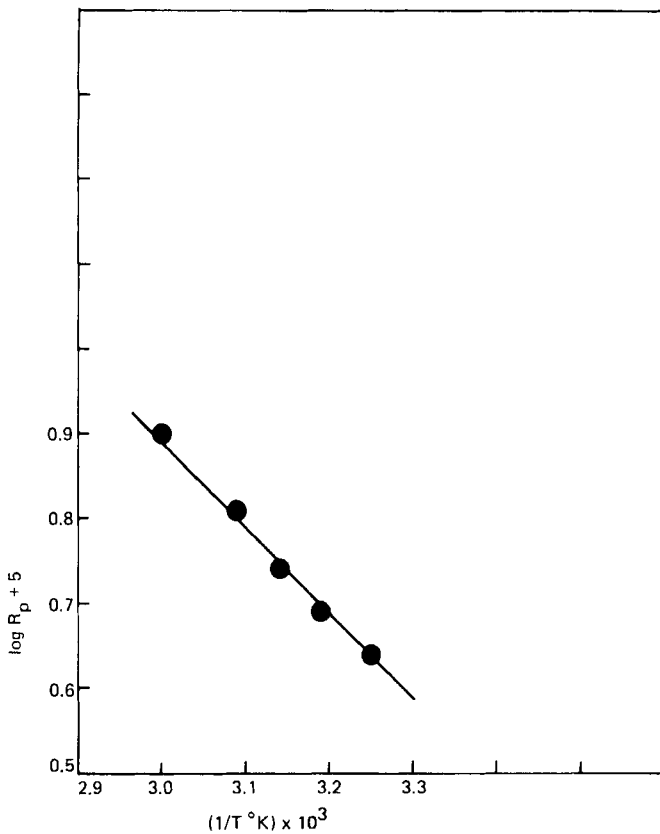
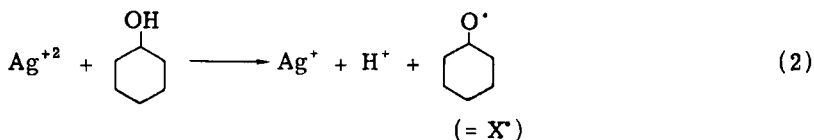
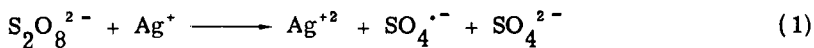


FIG. 5. Arrhenius plot of  $\log R_p$  vs  $1/T$ .

the literature [16-18] as being due to the decreased area of shielding of a strong hydration layer in nonaqueous media, which results in termination of the growing chain.

### MECHANISM

Based on the experimental orders, we suggest the following mechanism for the polymerization of acrylonitrile initiated by the redox system peroxydisulfate-cyclohexanol catalyzed by silver ion.



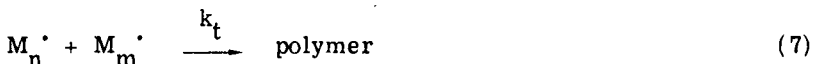
Initiation:



Propagation:



Termination:



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Accepted by editor July 27, 1983

Received for publication August 24, 1983