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Polymerization of Acrylonitrile Initiated by the Redox System, $K_2S_2O_8$-Citric Acid Catalyzed by Silver Ion

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ABSTRACT

The polymerization of acrylonitrile initiated by the redox system $K_2S_2O_8$-citric acid catalyzed by Ag^+ ion has been studied over the temperature range 35-50°C. The rate of polymerization is proportional to the square root of peroxydisulfate concentration. The initial rate increases with increasing citric acid concentration, but at relatively higher concentration of citric acid the rate decreases. The rate of polymerization also increases with increasing monomer concentration and temperature. The overall activation energy calculated from the Arrhenius plot was found to be 4.6 kcal/mole. On the basis of the observation, a suitable kinetic scheme has been proposed for the reaction.

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INTRODUCTION

The kinetics and mechanism of oxidation of several organic and inorganic substrates both under catalyzed by peroxydisulfate and uncatalyzed, has been of interest of several groups of workers [1-5]. That peroxydisulfate ion can initiate polymerization of certain vinyl monomers was reported by Bacon [6] as early as 1946. Peroxydisulfate ion, when coupled with monovalent silver ion, acts as a better initiator, since Ag^{2+} produced during the reaction is more powerful initiator than peroxydisulfate. Margon [7] reported the polymerization of acrylonitrile in aqueous solution initiated by a redox system such as peroxydisulfate with silver nitrate, sodium thiosulfate, and ferrous ammonium sulfate as reductant. Kern and co-workers [8] and Whitby et al. [9] reported the kinetics of the polymerization of acrolein initiated by peroxydisulfate-Ag^+ redox system. Recently Kagiya and co-workers [10] have reported the kinetic features of the redox polymerization of acrolein with the potassium persulfate-silver nitrate redox system. We have reported [11-18] the kinetics and mechanism of the redox polymerization of acrylonitrile initiated by several metal ions. In this present communication, we wish to report the polymerization of acrylonitrile initiated by the redox system $K_2S_2O_8$-citric acid catalyzed by silver ion (Ag^+).

EXPERIMENTAL

Acrylonitrile (American Cyanamid Co.) was washed with 5% NaOH, dilute H_3PO_4, and finally with water and dried over anhydrous $CaCl_2$. Peroxydisulfate, silver nitrate, and citric acid were from B. D. H. (Analar grade). All other reagents were Analar grade.

Pure distilled water, redistilled over alkaline potassium permanganate and free of carbon dioxide, was used throughout this investigation. As persulfate solutions are very susceptible to variation in impurities of the reacting solution, all the vessels used were of Jena glass.

The aqeuous acrylonitrile solution of definite molar concentration was prepared in a volumetric flask. A calculated amount of acrylonitrile together with water was introduced into a reaction vessel and thermostatted. To that the required quantity of silver nitrate and citric acid were introduced. The polymerization was initiated by adding known amounts of freshly prepared standard solution of $K_2S_2O_8$. Several samples were withdrawn after desired intervals of time and introduced directly into beakers containing 10 ml of cooled 1% hydroquinone solution in $2\underline{N}$ H_2SO_4 to stop the polymerization.

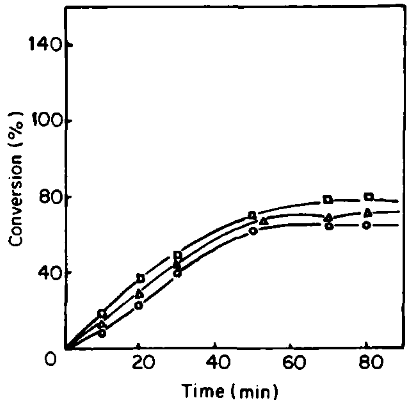

FIG. 1. Plots of percentage conversion vs. time effect of oxidant concentration: (○) [$K_2S_2O_8$] = 0.01 M, (△) [$K_2S_2O_8$] = 0.02 M, (□) [$K_2S_2O_8$] = 0.03 M. [AN] = 0.754 M; [CA] = 0.002 M; [Ag^+] = 0.001 M; 35°C.

RESULTS AND DISCUSSION

Dependence of Rate on Peroxydisulfate Concentration

The initial rate and the limiting conversion tend to increase with increasing peroxydisulfate concentration at a fixed concentration of activator and monomer [Fig. 1]. Since neither citric acid nor silver nitrate alone could initiate polymerization under any circumstances, it is the quantity of the reactive species [$CA^\cdot$, $SO_4^{\cdot -}$], produced by the interactions of peroxydisulfate, Ag^+, and citric acid (CA) which affect the initial polymerization rate. The double logarithmic plot of the initial rate R_i (taken from the slopes of the conversion curves at zero time and expressed in percent conversion per minute) vs. the peroxydisulfate concentration [Fig. 2] determines the order of reaction with respect to the catalyst concentration. The slope was computed to be 0.5. Similar results have been reported by various workers [19-21] who have shown that the rate of peroxide-catalyzed vinyl polymerization in homogeneous systems if proportional to the square root of the peroxydisulfate concentration. In terms of generally accepted kinetic interpretation this means that the termination process occurs by mutual collision of the two active centers and that the steady-state approximation is reasonably well fulfilled.

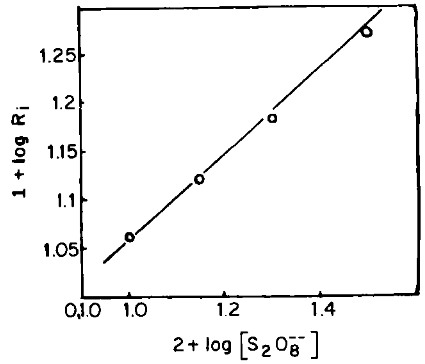

FIG. 2. Double logarithmic plot of the initial rate of polymerization (R_i) vs. concentration of [$K_2S_2O_8$].

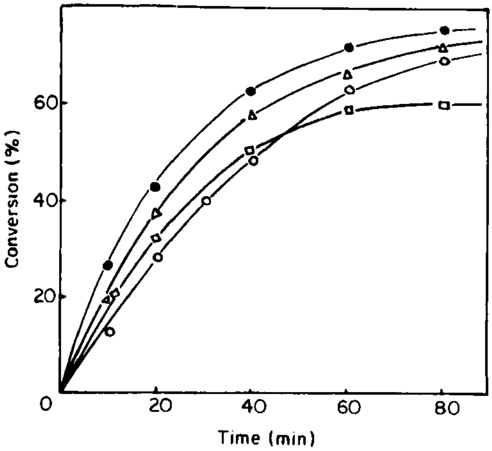

FIG. 3. Plots of percentage conversion vs. time effect of activator concentration [CA]: (○) [CA] = 0.5 × 10^{-3} M; (△): [CA] = 1.5 × 10^{-3} M; (●) [CA] = 3.5 × 10^{-3} M; (□) [CA] = 5 × 10^{-3} M. [$K_2S_2O_8$] = 0.02 M; [AN] = 0.754 M; [Ag^+] = 0.001 M; 35°C.

Rate of Dependence on Activator Concentration

The initial rate and the limiting conversion have been found to increase with increasing activator concentration within the range of a 5 × 10^{-4}-5 × 10^{-3} M (Fig. 3). At relatively higher concentrations of citric acid (5×10^{-3} M), however, an appreciable decrease in the initial rate and in the maximum conversion is observed. This observation agrees with the observations made by Morgan [7] and by Guha [22] on similar systems with oxyacid of sulfur as the activator.

In general, an enhancement in the rate of polymerization in a redox initiated system is expected with increasing concentration of activator (citric acid) while H^+ ions play an important role in decreasing the rate of polymerization.

$$CA^{\cdot} + S_2O_8^{2-} \longrightarrow CA + SO_4^{2-} + \dot{S}O_4^{-}$$

$$CA^{\cdot} + \dot{S}O_4^{-} \longrightarrow CA + SO_4^{2-} + H^+$$

At higher concentrations of citric acid, the rate of generation as well as the concentration of reactive species is suppressed because of the increased concentration of hydrogen ions.

Effect of Monomer Concentration

Figure 4 illustrates the influence of monomer concentration on the rate of polymerization. The rate of polymerization increases linearly with increase of monomer concentration up to 0.75 M, and then with further increase of AN the rate of polymerization decreases. The decrease in the rate of polymerization at higher monomer concentration might be due to a gel effect, i. e., an increase in medium due to solubility of polyacrylonitrile in its own monomer would be more pronounced at higher monomer concentrations. This hinders termination, and hence the polymerization rate decreases.

Effect of Temperature

The effect of temperature on the rate of polymerization is shown In Fig. 5. The initial rate as well as the limiting conversion increases with increasing temperature in the range 35-50°C. The overall activation energy has been calculated from the Arrhenius plot (Fig. 6) to be 4.6 kcal/mole.

Effect of Organic Solvents

The introduction of water-miscible organic solvents like methanol, acetone, or dimethylformamide tends to depress the initial rate as well as limiting conversion. The decrease in the rate of polymerization could be interpreted by assuming that the water-miscible organic

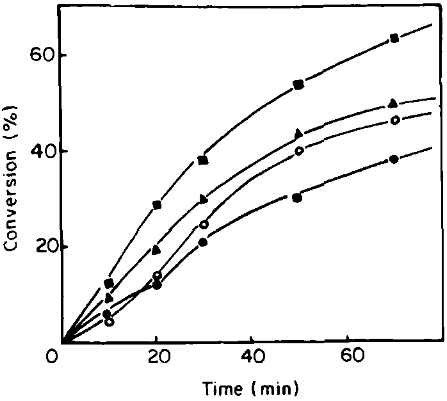

FIG. 4. Plots of percentage conversion vs. time effect of monomer concentration [M]: (●) [AN] = 0.301 M; (▲) [AN] = 0.452 M; (■) [AN] = 0.754 M; (○) [AN] = 0.905 M [$K_2S_2O_8$] = 0.021 M; [CA] = 0.002 M; [Ag^+] = 0.001 M; 35°C.

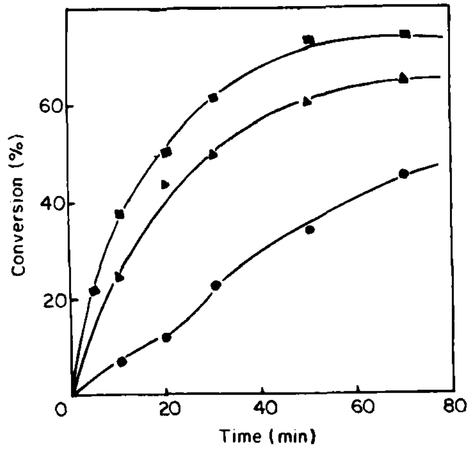

FIG. 5. Plots of percentage of conversion vs. time effect of temperature: (●) 35°C; (▲) 45°C; (■) 50°C. [$K_2S_2O_8$] = 0.02 M; [CA] = 0.004 M; [AN] = 0.754 M; [Ag^+] = 0.001 M.

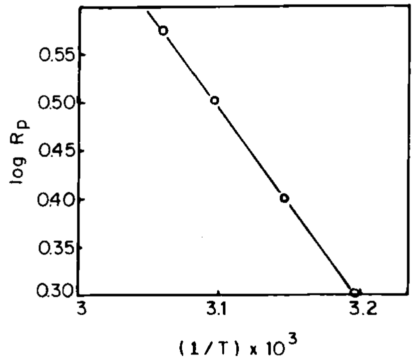

FIG. 6. Arrhenius plot for the initial rate of polymerization.

solvents can perform three functions: (a) the decrease of the area of shielding of a strong hydration layer in aqueous medium results in the termination of the growing chain, (b) the increase of the regulated rate of production of primary radicals, which renders the termination rate relatively fast compared to the growing rate, in accordance with the views of Kern et al. [23], (c) the interchain hydrogen bonding interlocking the polymer chain is not rigid, as a result of which the tendency for mutual termination of the polymer chains occurs.

MECHANISM

The proposed mechanism involves the interaction between peroxydisulfate and silver ions producing Ag^{+2} and $SO_4^{\bullet -}$. Since it is known that the reaction between persulfate and silver ions is second order, it is probable that this reaction is the controlling factor in this system. In the second step, divalent silver reacts with citric acid producing citrate radicals. Hence citrate ($CA^{\bullet}$) and sulfate ion radicals ($SO_4^{\bullet -}$) are the active species which initiate polymerization. According to Roskin [24], hydroxyl radicals ($OH^{\bullet}$) were also possible initiating radicals in this system. This was not, however, observed from endgroup analysis. The hydroxyl endgroup in peroxydisulfate-initiated polymerization might arise from the hydrolysis of sulfate endgroups in polymer chains.

The mechanism for the system may be represented as shown in Eqs. (1)-(5).

Decomposition:

$$S_2O_8^{2-} + Ag^{+} \longrightarrow SO_4^{-} + SO_4^{-2} + Ag^{2+} \tag{1}$$

$$Ag^{2+} + CA \longrightarrow \dot{C}A + H^{+} + Ag^{+} \qquad (2)$$

$$(\dot{C}A \text{ or } S\dot{O}_4^{-} = R^{\bullet})$$

Initiation:

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet} \qquad (3)$$

Propagation:

$$RM^{\bullet} + M \xrightarrow{k_p} RM_i^{\bullet} \qquad (4a)$$

$$\vdots$$

$$RM_{n-1}^{\bullet} + M \xrightarrow{k_p} RM_n^{\bullet} \qquad (4b)$$

Termination

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_{tr}} \text{Polymer.} \qquad (5)$$

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