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### Thiols as Reducing Agents. 1. Polymerization of Acrylonitrile Initiated by the Peroxydisulfate-Thiomalic Acid Redox System

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NOTE

## Thiols as Reducing Agents. I. Polymerization of Acrylonitrile Initiated by the Peroxydisulfate-Thiomalic Acid Redox System

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### ABSTRACT

The aqueous polymerization of acrylonitrile (AN) initiated by the potassium persulfate-thiomalic acid (TMA) redox system has been studied at  $35 \pm 0.1^\circ\text{C}$  in a nitrogen atmosphere. The rate of polymerization is governed by the expression,  $R_p = K[\text{AN}] [\text{S}_2\text{O}_8^{2-}]^x [\text{TMA}]^{0.40}$ , where  $x = 0.60$  for lower monomer concentration and  $0.75$  for higher monomer concentration. The overall activation energy was found to be  $7.3 \text{ kcal/mol}$  in the investigated range of temperature. The deviations from normal kinetics are discussed, and a tentative mechanism of initiation is given. The effects of inorganic electrolytes on polymerization were also investigated.

Mercaptans have been reported to form good redox pairs for vinyl polymerization. The use of  $\alpha$ -mercaptocarboxylic acids as redox components is, however, recent [1-6]. This communication presents the results of the polymerization of acrylonitrile initiated by the redox system peroxydisulfate-thiomalic acid,

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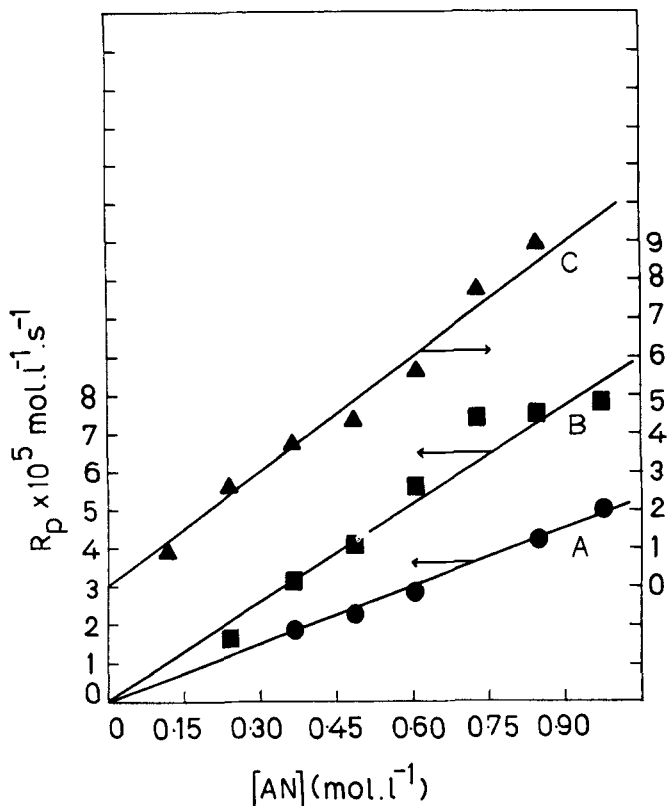


FIG. 1. Plot of  $R_p$  vs  $[AN]$ .  $[TMA] = 1.2 \times 10^{-2}$  mol/L, time = 45 min.  $[S_2O_8^{2-}]$ : (A) =  $5.0 \times 10^{-3}$  mol/L, (B) =  $1.0 \times 10^{-2}$  mol/L, (C) =  $1.5 \times 10^{-2}$  mol/L.

The polymerization procedure has been described elsewhere [7]. A very small induction period was noticed throughout the experiments.

The monomer concentration was varied over the range 0.1215 to 0.9716 mol/L at fixed concentrations of the initiator of  $5.0 \times 10^{-3}$ ,  $1.0 \times 10^{-2}$ , and  $1.5 \times 10^{-2}$  mol/L at 35°C. Plots of  $R_p$  vs  $[AN]$  are linear (Fig. 1) and pass through the origin, indicating that the order with respect to monomer is unity.

The rate of polymerization was investigated by varying the peroxydisulfate concentration over the range  $2.0 \times 10^{-3}$  to  $2.0 \times 10^{-2}$  mol/L at different concentrations of acrylonitrile. The initiator exponent was found to be 0.60 at the monomer concentration 0.3036 mol/L (Fig. 2, Plot A), and 0.75 at higher monomer concentrations

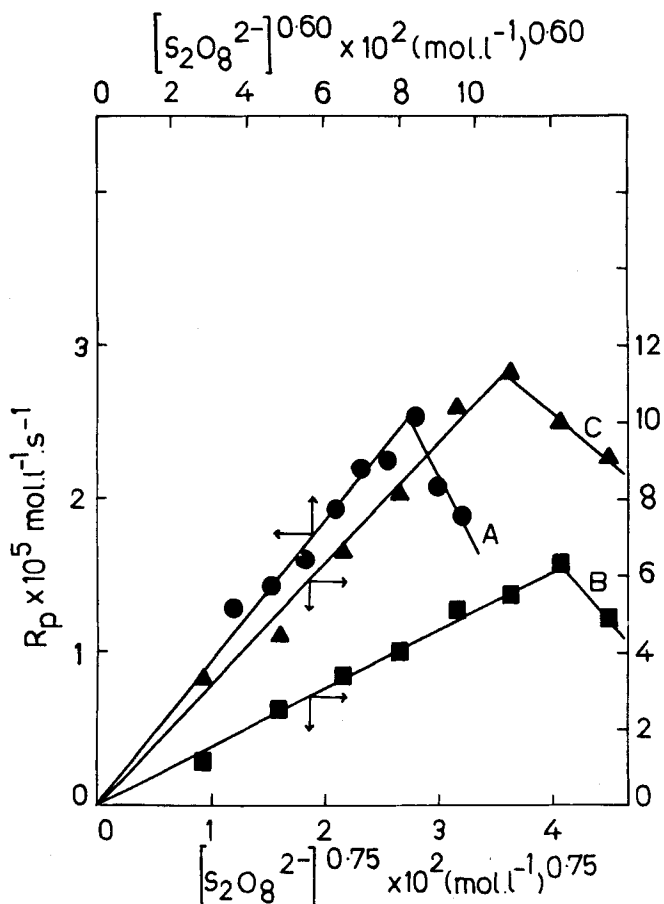
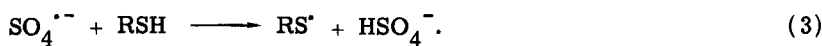


FIG. 2. Plot of  $R_p$  vs  $[S_2O_8^{2-}]^{0.60}$ ,  $[TMA] = 1.2 \times 10^{-2}$  mol/L, time = 45 min,  $[AN]$ : (A) = 0.3036 mol/L.  $R_p$  vs  $[S_2O_8^{2-}]^{0.75}$ ,  $[TMA] = 1.2 \times 10^{-2}$  mol/L, time = 45 min,  $[AN]$ : (B) = 0.6073 mol/L, (C) = 0.9109 mol/L.

(0.6073 and 0.9109 mol/L, Fig. 2, Plots B and C). An order of 0.60, 0.75, and 0.75 with respect to the initiator obtains below the concentrations of peroxydisulfate of  $1.6 \times 10^{-2}$ ,  $1.4 \times 10^{-2}$ , and  $1.2 \times 10^{-2}$  mol/L, respectively, after which the rate of polymerization shows a decreasing trend. Generally, a negative trend in the rate with respect to the initiator indicates its participation in termination reactions. The number of growing chain radicals increased at higher

concentrations of peroxydisulfate, and thus termination took place easily. We suggest that (1) either the rate of radical generation in our system became almost independent of the peroxydisulfate concentration beyond the limit described above, (2) or the increase in the ionic strength of the medium due to the increase in the concentration of peroxydisulfate led to incipient coagulation, which in turn brought down the number of polymer particles, thereby affecting the rate of polymerization.

The deviation to a slightly higher order (0.60 and 0.75) with respect to the initiator concentration is indicative of mixed termination, linear and quadratic, with the latter predominating [3]. A slight increase in the order with respect to the initiator is due to change in density of polymer particles in the reaction mixture. The contribution of the thermal homolysis of peroxydisulfate to the production of  $\text{SO}_4^{\cdot-}$  is assumed to be negligible (Eq. 1), since it would require an activation energy higher than that observed for the overall polymerization (7.3 kcal/mol). The sulphydryl radical derived from thiomalic acid is assumed to be the predominant initiating species. We suggest a plausible mechanism of initiation.



The plots of  $R_p$  vs  $[\text{TMA}]^{0.40}$  are linear (Fig. 3), indicating 0.40-order dependence on TMA concentration in the range  $2.0 \times 10^{-3}$  to  $1.6 \times 10^{-2}$  mol/L of TMA. Because TMA is a tribasic acid [8], it dissociates to release protons in solution, which in turn catalyzes the conversion of peroxydisulfate into  $\text{HSO}_4^-$ ,  $\text{SO}_3$ , and molecular oxygen [9]. Thus the effective concentration of peroxydisulfate was decreased and hence a decrease in the rate of radical generation might be expected to lead to an anomalous order. We have already reported similar effects [7, 10].

The temperature was varied from 25 to 45°C. From the slope of the Arrhenius plot (Fig. 4), the overall activation energy was calculated to be 7.3 kcal/mol. The addition of inorganic electrolytes, such as NaCl, KCl,  $\text{Na}_2\text{SO}_4$ , and  $\text{MgSO}_4$ , lowered the rate of polymeriza-

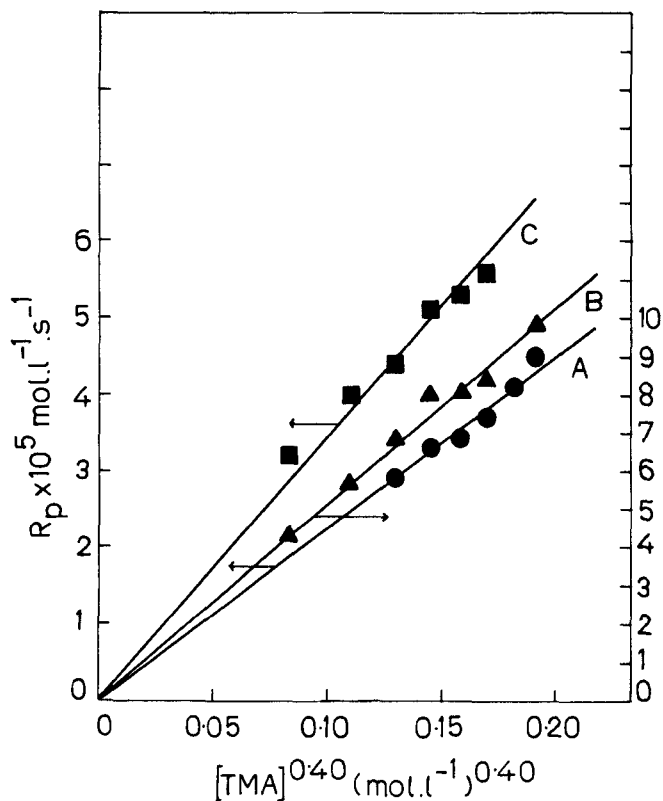


FIG. 3. Plot of  $R_p$  vs  $[TMA]^{0.40}$ .  $[AN] = 0.9109$  mol/L, time = 45 min.  $[S_2O_8^{2-}]$ : (A) =  $5.0 \times 10^{-3}$  mol/L, (B) =  $1.0 \times 10^{-2}$  mol/L, (C) =  $1.5 \times 10^{-2}$  mol/L.

tion due to the dissociation of the electrolyte with the consequent increase in the ionic strength of the medium and the premature termination of the growing polymer chains. However,  $MnSO_4$  increased the rate because  $Mn^{2+}$  ions are known to autocatalyze the initiating reaction.

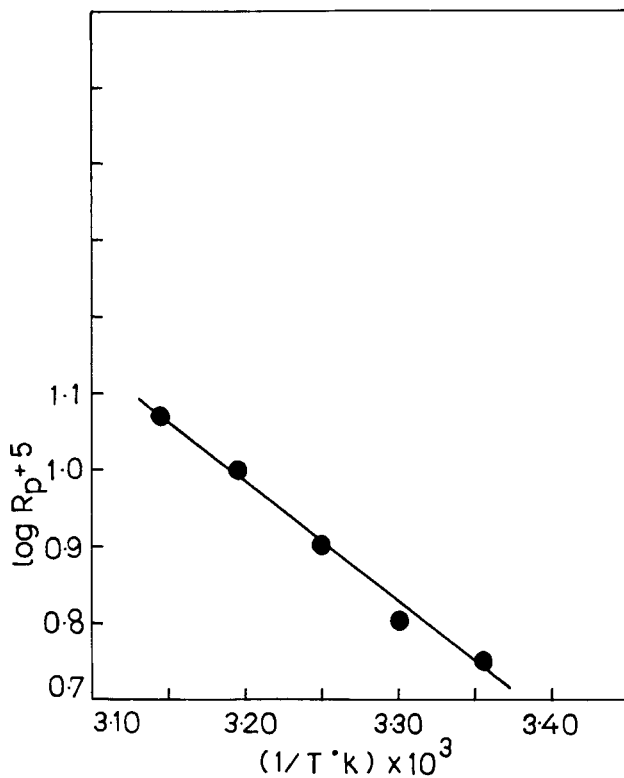


FIG. 4. Arrhenius plot of  $\log R_p$  vs  $1/T$ .

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