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Thiols as Reducing Agents. II. Polymerization of Acrylonitrile Initiated by the Bromate-Thiomalic Acid Redox System

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NOTE

THIOLS AS REDUCING AGENTS. II. POLYMERIZATION OF ACRYLONITRILE INITIATED BY THE BROMATE–THIOMALIC ACID REDOX SYSTEM

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Thiols find application as chain regulators in redox-initiated vinyl polymerization in order to prepare polymers and copolymers to suit specific requirements. Their use as redox components in conjunction with bromate is, however, recent [1-4]. As a part of our investigation [5], we present the results of the polymerization of acrylonitrile initiated by the bromate-thiomalic acid redox system.

Monomer purification and the polymerization procedures were the same as reported earlier [5]. The polymerization started almost instantaneously without any induction period.

Figure 1 illustrates the dependence of the polymerization rate on bromate concentration. The study was made in the range 0.4-1.8 mmol/L of bromate concentration at monomer concentrations of 0.3036, 0.6073, and 0.9109 mol/L. The initiator exponent was found to be 0.5 (Plot A) and 0.4 (Plots B and C), below bromate concentrations of 1.4, 1.2, and 1.6 mmol/L, respectively. Above these concentrations the rate of polymerization showed a decreasing trend, possibly because the high concentration of initiator affects the

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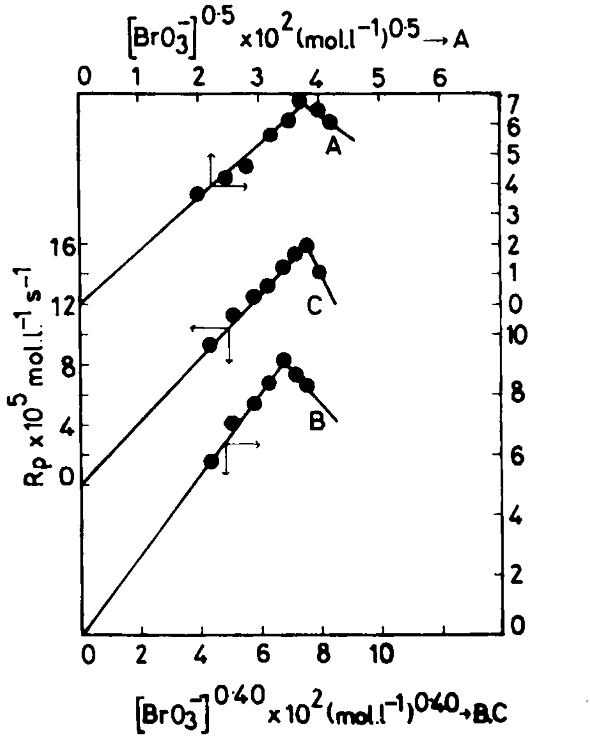

FIG. 1. Plot of R_p vs $[BrO_3^-]^{0.5}$ and $[BrO_3^-]^{0.4}$. $[H^+]$ = 10 mmol/L. [TMA] = 1.0 mmol/L. [AN] : (A) = 0.3036 mol/L, (B) = 0.6073 mol/L, (C) = 0.9109 mol/L.

colloidal stability of the system and may bring about a decrease in molecular weight. Similar observations have been reported by Evans et al. [6]. While the 0.5 order with respect to catalyst concentration shows that the termination occurs by mutual interaction of the growing radicals, a slight decrease to a value below 0.5 indicates the wastage of radicals in the termination step due to some side reactions [7].

The rate of polymerization increases with increasing thiomalic acid in the range 0.4-1.6 mmol/L at three different concentrations of bromate. Plots of R_p vs $[TMA]^{0.5}$ are linear (Fig. 2), indicating a half-order dependence on thiomalic acid concentration which also supports mutual termination of growing chain radicals.

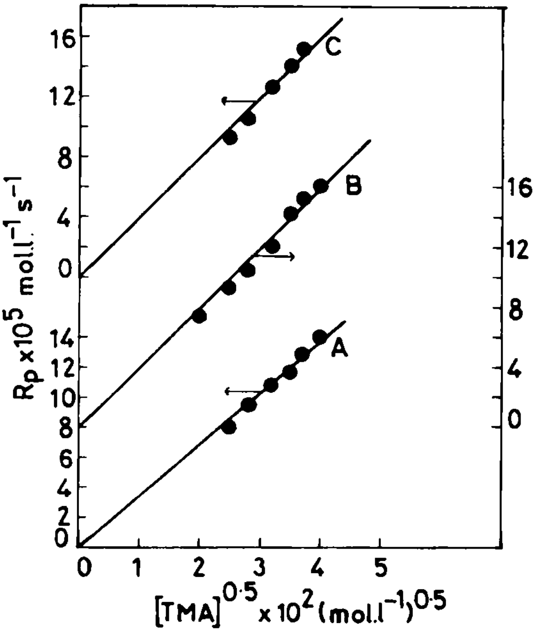

FIG. 2. Plot of R_p vs $[TMA]^{0.5}$. $[H^+]$ = 10 mmol/L. [AN] = 0.9109 mol/L. $[BrO_3^-]$: (A) = 0.6 mmol/L, (B) = 1.0 mmol/L, (C) = 1.6 mmol/L.

The rate of polymerization was investigated by varying the monomer concentration over the range 0.1215-0.9716 mol/L at bromate concentrations of 0.6, 1.0, and 3.0 mmol/L, keeping the thiomalic acid concentration constant. Plots of R_p vs [AN] are linear (Fig. 3) and pass through the origin, indicating that the order with respect to monomer is unity. Thus we can infer a standard free-radical polymerization initiated by thiomalate free-radical.

The effect of temperature on the polymerization rate was studied in the range 30-45°C. The overall energy of activation, as calculated from the Arrhenius plot (Fig. 3, Plot D), was 4.6 kcal/mol within the temperature range 25-35°C. However, a linear increase in the rate was not observed beyond 35°C, and the rate remained almost constant. This may probably be due to a good portion of the primary radicals being destroyed at higher temperature by side reactions. Similar reasoning has been reported by other workers [8].

The addition of inorganic electrolytes, such as KCl and $MgSO_4$, depressed the polymerization rate due to the ionic dissociation of the added electrolytes

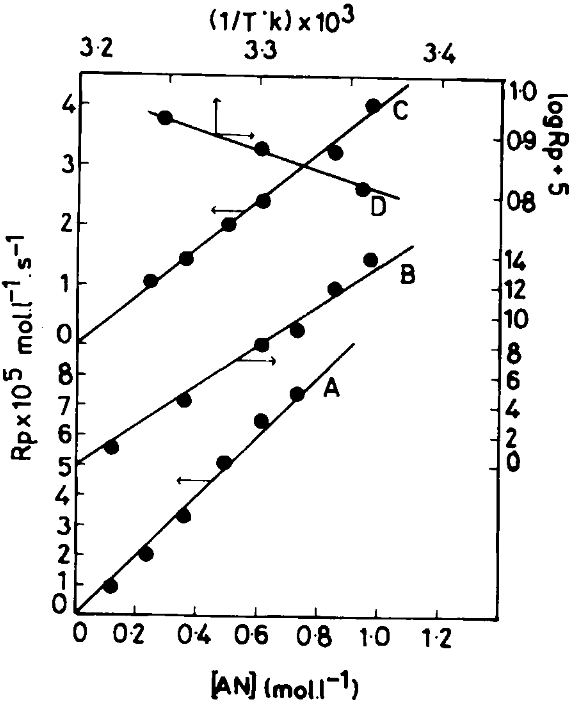

FIG. 3. Plot of R_p vs [AN]. [H^+] = 10 mmol/L. [TMA] = 1.0 mmol/L. [BrO_3^-] : (A) = 0.6 mmol/L, (B) = 1.0 mmol/L, (C) = 3.0 mmol/L, (D) = Arrhenius plot of log R_p vs $1/T$.

which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chains [5].

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