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Aqueous Polymerization of Acrylonitrile Initiated by Potassium Bromate-Thioacetamide Redox System

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ABSTRACT

The polymerization of acrylonitrile initiated by potassium bromate coupled with thioacetamide was investigated in aqueous solution under nitrogen atmosphere. The effect of monomer, initiator, activator, and acid concentration on the rate of polymerization as well as on maximum conversion was evaluated. The rate of polymerization was found to increase up to 1.25×10^{-3} M of initiator concentration and thereafter it decreased. The rate of polymerization also increased with the monomer and activator concentration up to 1.5078 and 4.0×10^{-3} M, respectively, after which the rate fell. The effect of acid concentration, temperature, and solvents on rate of polymerization has been studied and a suitable kinetic scheme has been pictured.

INTRODUCTION

During the past several years, vinyl polymerization initiated by redox systems has been extensively studied by several groups of workers [1-11]. Nayak et al. [12-21] have reported aqueous polymerization of vinyl monomers initiated by a multitude of redox systems

including many metal and nonmetal ions. Potassium bromate alone cannot initiate polymerization, but, coupled with a suitable substrate, it acts as an efficient initiator for vinyl polymerization. Earlier, we have reported [22, 23] aqueous polymerization initiated by the bromate-thiourea redox system.

This communication presents the results of aqueous polymerization of acrylonitrile initiated by the bromate-thioacetamide redox system.

EXPERIMENTAL

Acrylonitrile from Koch-Light Laboratories was purified according to the method of Bamford et al. [24]. Potassium bromate and thioacetamide (A.R.) were used as such. Water distilled twice over alkaline permanganate and deionized by passing it through a column of Biodeminrolit resin (Permutit Co., United Kingdom) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing it through several columns of Fisser's solution, saturated lead acetate solution, and finally through a wash bottle containing distilled water.

The polymerization was carried out according to our previous procedure [23] by using required concentrations of initiator, monomer, acid, and activator.

DISCUSSION

Rate Dependence on Activator Concentration

The variation of percentage conversion with time at different concentrations of thioacetamide is shown in Fig. 1. The rate of polymerization as well as the maximum conversion was found to increase with an increase of thioacetamide concentration from 1×10^{-3} to 3×10^{-3} M after which a decreasing trend was noticed. By increasing the concentration of the activator, a large number of free radicals is produced, thereby increasing the rate of polymerization. But, beyond 3×10^{-3} M thioacetamide concentration, the free radicals produced might be participating in the termination reaction, thereby decreasing the rate of polymerization.

Rate Dependence on the Initiator Concentration

Figure 2 shows the percentage conversion data at varying concentrations of the initiator and at a fixed concentration of the activator and monomer. There is a rapid enhancement of the rate of polymerization as well as the maximum conversion with an increase in the

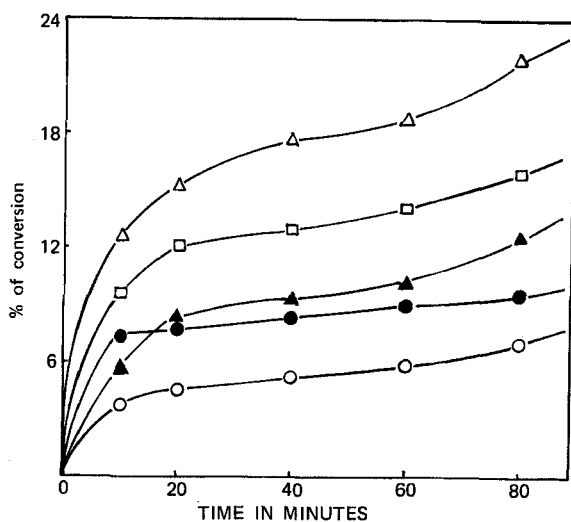


FIG. 1. Plots of conversion percentage versus time at different activator concentrations: $[\text{KBrO}_3] = 5 \times 10^{-3} \text{ M}$, $[\text{H}^+] = 0.05 \text{ M}$, $[\text{AN}] = 0.7539 \text{ M}$, temperature = 35°C . $[\text{TA}]$: (○) $1 \times 10^{-3} \text{ M}$, (●) $2 \times 10^{-3} \text{ M}$, (△) $3 \times 10^{-3} \text{ M}$, (□) $4 \times 10^{-3} \text{ M}$, (▲) $6 \times 10^{-3} \text{ M}$.

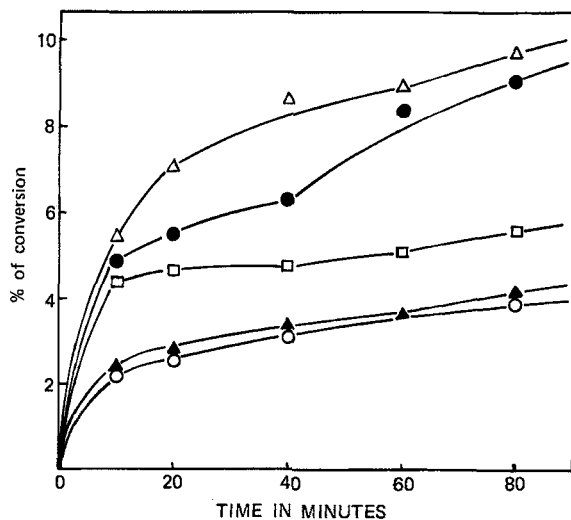


FIG. 2. Plots of conversion percentage versus time at different initiator concentrations: $[\text{TA}] = 1 \times 10^{-2} \text{ M}$, $[\text{H}^+] = 0.05 \text{ M}$, $[\text{AN}] = 0.7539 \text{ M}$, temperature = 35°C . $[\text{KBrO}_3]$: (○) $1.25 \times 10^{-3} \text{ M}$, (●) $2.5 \times 10^{-3} \text{ M}$, (△) $5 \times 10^{-3} \text{ M}$, (□) $10 \times 10^{-3} \text{ M}$, (▲) $25 \times 10^{-3} \text{ M}$.

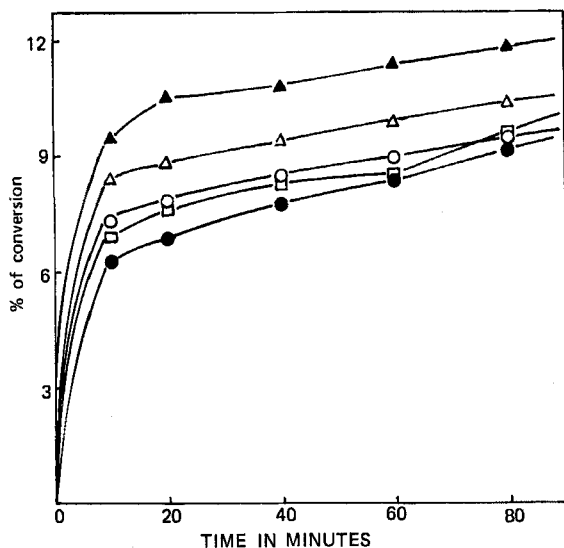


FIG. 3. Plots of conversion percentage versus time at different monomer concentrations: $[\text{KBrO}_3] = 5 \times 10^{-3} \text{ M}$, $[\text{H}^+] = 0.05 \text{ M}$, $[\text{TA}] = 1 \times 10^{-2} \text{ M}$, temperature = 35°C . $[\text{AN}]$: (\bullet) 0.3769 M , (\circ) 0.7539 M , (Δ) 1.1308 M , (\blacktriangle) 1.5078 M , (\square) 2.2617 M .

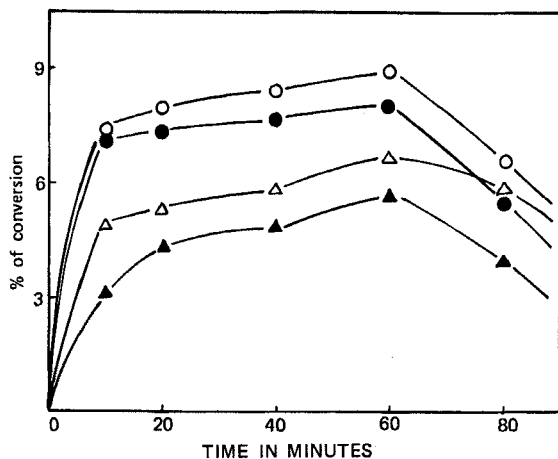


FIG. 4. Plots of conversion Percentage versus time at different sulfuric acid concentrations: $[\text{KBrO}_3] = 5 \times 10^{-3} \text{ M}$, $[\text{AN}] = 0.7539 \text{ M}$, $[\text{TA}] = 1 \times 10^{-2} \text{ M}$, temperature = 35°C . $[\text{H}^+]$: (\bullet) $2.5 \times 10^{-2} \text{ M}$, (\circ) $5.0 \times 10^{-2} \text{ M}$, (Δ) $15.0 \times 10^{-2} \text{ M}$, (\blacktriangle) $25 \times 10^{-2} \text{ M}$.

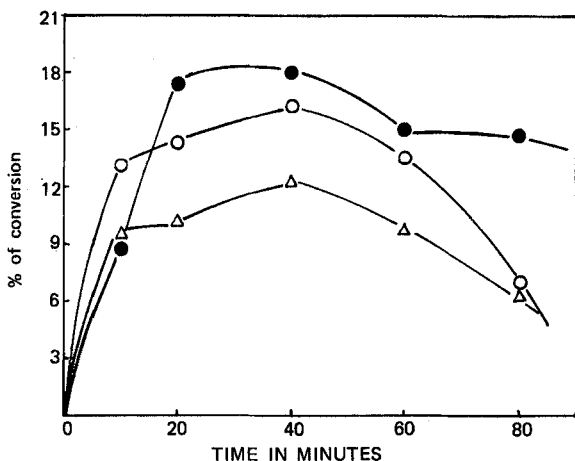


FIG. 5. Plots of conversion percentage versus time in the presence of water-soluble organic solvents: $[\text{KBrO}_3] = 5 \times 10^{-3} \text{ M}$, $[\text{TA}] = 1 \times 10^{-2} \text{ M}$, $[\text{AN}] = 0.7539 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.05 \text{ M}$, temperature = 35°C . (●): $[\text{CH}_3\text{OH}] = 5\% \text{ v/v}$, (○) $[\text{C}_3\text{H}_7\text{OH}] = 5\% \text{ v/v}$, (△) $[\text{C}_4\text{H}_9\text{OH}] = 5\% \text{ v/v}$.

bromate ion concentration from 1.25×10^{-3} to $5.0 \times 10^{-3} \text{ M}$, after which it decreases. Such observations can be explained by considering the termination mechanism. At higher concentrations of the bromate ion, a large number of primary radicals is produced which might participate in the termination reaction. Thus the percentage conversion decreases. Similar explanations have been observed by Palit et al. [25] and Nayak et al. [23].

Rate Dependence on Monomer Concentration

A typical set of percentage conversion curves at different monomer concentrations is shown in Fig. 3. The monomer concentration was varied from 0.3769 to 2.2612 M. The rate of polymerization as well as the percentage conversion was found to increase progressively with increasing monomer concentration from 0.3769 to 1.5078 M and thereafter it decreased. The initial increase in the rate of polymerization might be due to the production of a large number of primary radicals which propagate at a faster rate, causing the polymerization. At higher concentrations of the monomer the decrease in the rate of polymerization might be due to the gel effect [26], i.e., an increase in the viscosity of the medium owing to the solubility of the polymer in its own monomer. This retards the rate of diffusion of monomer and initiator into the growing chains, and for polymerization to occur.

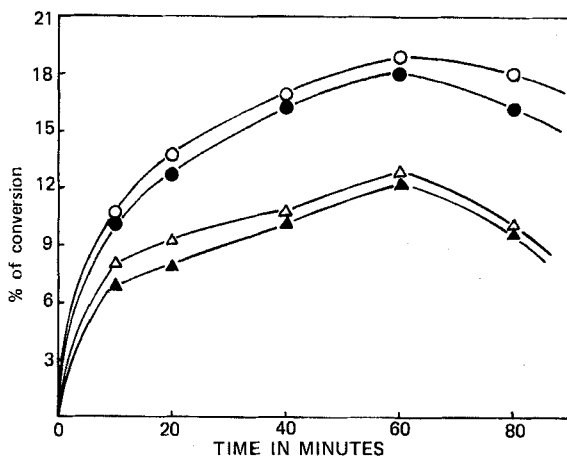


FIG. 6. Plots of conversion percentage versus time in the presence of some inorganic salts: $[\text{KBrO}_3] = 5 \times 10^{-3} \text{ M}$, $[\text{AN}] = 0.7539 \text{ M}$, $[\text{TA}] = 1 \times 10^{-2} \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.05 \text{ M}$, temperature = 35°C . (●): $[\text{KCl}] = 0.01 \text{ M}$, (○): $[\text{NaF}] = 0.01 \text{ M}$, (△) $[\text{Na}_2\text{SO}_4] = 0.01 \text{ M}$, (▲) $[\text{MnSO}_4] = 0.01 \text{ M}$.

Effect of Acid Concentration

The effect of acid concentration on the rate of polymerization was studied by varying the concentration of sulfuric acid from 2.5×10^{-2} to $25 \times 10^{-2} \text{ M}$ (Fig. 4). The rate of polymerization as well as the maximum conversion was found to increase with acid concentration from 2.5×10^{-2} to $5.0 \times 10^{-2} \text{ M}$ and thereafter it decreased. At lower concentrations of the acid the latter is mostly utilized in converting thioacetamide to isothioacetamide, thus facilitating the formation of isothioacetamido radical with greater ease. Therefore, the rate of polymerization increases. At lower pH the large number of primary radicals which is formed might terminate the growing chains. Second, at lower pH some species might be formed which might act as radical scavengers, thereby decreasing the rate of polymerization.

Effect of Organic Solvents

The addition of (5% v/v) water-miscible organic solvents like methanol, propanol, and butanol depresses the initial rate as well as the maximum conversion (Fig. 5). Since these solvents differ in their miscibility with the monomer, the formation of solvent radicals from the primary radicals, the contribution of the solvent radicals in the propagation step, and the participation of the solvent radicals in the

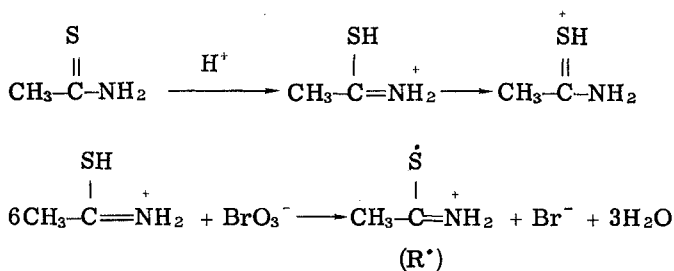
termination of the growing chains, there is a large variation in their percentage conversion. Again, these solvents might decrease the area of shielding of a strong hydration layer in aqueous media, resulting in the termination of the radical end of the growing chains. These solvents increase the regulated production of primary radicals which, under the existing experimental conditions, renders the termination rate relatively fast compared to the rate of growth of the polymer chains, as pointed out by Kern et al. [27].

Effect of Inorganic Salts

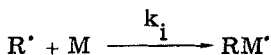
The rate of polymerization has been evaluated in the presence of 0.02 M neutral inorganic salts such as KCl, Na₂SO₄, MnSO₄, and NaF at a fixed concentration of all other reagents (Fig. 6). The addition of KCl and Na₂SO₄ depresses the initial rate and maximum conversion. This might be due to the ionic dissociation of the added electrolyte, which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chain.

Reaction Mechanism and Rate Law

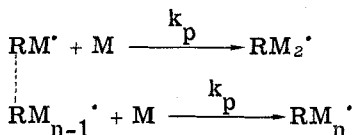
In the initiating system consisting of bromate, acid, thioacetamide, and monomer, the free radicals can be formed in the following manner.



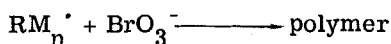
Initiation:



Propagation:



Termination:



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