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Polymerization of Methacrylamide Initiated by the Persulfate/Thiolactic Acid Redox System

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ABSTRACT

The aqueous polymerization of methacrylamide initiated by the ammonium persulfate/thiolactic acid redox system has been studied at 35 ± 0.2°C. The rate of polymerization is governed by the expression, $R_p = K_p[\mathrm{MAA}]^{1.33}[\mathrm{TLA}]^{0.22}$ $[\text{ammonium persulfate}]^{0.6}$. The deviations from normal kinetics are discussed. A tentative mechanism of initiation is given. The temperature dependence of the rate of polymerization has been studied over the range 30-55°C. The overall activation energy of polymerization is 10.4 kcal/mole.

In recent studies various thiols have been used as the redox component to initiate the polymerization of methyl methacrylate and acrylamide [1-4]. The present paper reports the results of the aqueous polymerization of methacrylamide initiated by the ammonium persulfate/thiolactic acid initiator system at 35 ± 0.2°C in nitrogen.

The polymerization was followed by the quantitative estimation of double bonds in methacrylamide [6, 7]. A short variable induction period was observed in almost all experiments. Graphs were plotted after eliminating the induction periods.

A plausible mechanism of initiation may be given by Eqs. (1)-(4).

$$S_2O_8^{2-} \longrightarrow 2\,\dot{S}O_4^- \tag{1}$$

$$S_2O_8^{2-} + RSH \longrightarrow \dot{S}O_4^- + R\dot{S} + HSO_4^- \tag{2}$$

$$\dot{S}O_4^- + RSH \longrightarrow R\dot{S} + HSO_4^- \tag{3}$$

$$R\dot{S} + M \longrightarrow \dot{M} \tag{4}$$

The homolytic fission of peroxydisulfate [Eq. (1)] is assumed to be negligible, since the overall activation energy observed in this study (10.4 kcal/mole) is far less than that (18.4 kcal/mole) reported for methacrylamide polymerization initiated by persulfate alone [8].

The dependence of polymerization rate on the catalyst concentration is shown in Fig. 1. The catalyst exponent is 0.6. The deviation to a slightly higher value is indicative of mixed termination, linear and quadratic, with the latter predominating.

There is a nominal increase in the rate of polymerization with increase in the concentration of thiolactic acid (Fig. 2). The corresponding value for the exponent in thiolactic acid is 0.22. Thiolactic acid presumably participates in side reactions which partially undo its activating effect. In the aqueous phase, the equilibrium (5) becomes significant.

$$CH_3CH(SH)COOH \xrightleftharpoons{K} CH_3CH(SH)COO^- + H^+ \tag{5}$$

This causes a decrease in the pH of the medium with increase in the concentration of thiolactic acid. The hydrogen ions may catalyze the decomposition of persulfate by a non-free-radical mechanism [9]. Thus the effective concentration of persulfate decreases with increasing thiolactic acid concentration. Decreasing the initial pH of the medium (by adding sulfuric acid) decreases the rate of polymerization. Similar side reactions involving hydrogen ions were given to explain the behavior of activator in the polymerization of methacrylamide initiated by the persulfate/ascorbic acid system [10].

The reaction profiles as a function of monomer concentration is shown in Fig. 3. The corresponding value of monomer exponent is 1.33. The first-order dependence of rate on monomer concentration

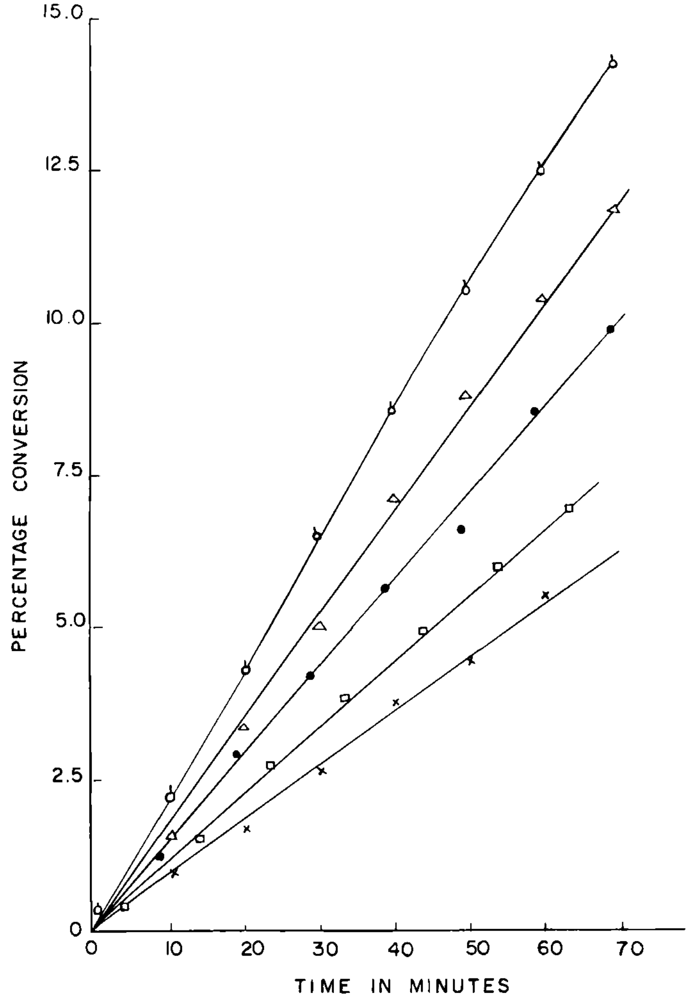

FIG. 1. Plot of initial course of polymerization for various initial concentrations of ammonium persulfate: (×) [$(NH_4)_2S_2O_8$] = 3.76 × 10^{-3} mole/liter; (□) [$(NH_4)_2S_2O_8$] = 5.84 × 10^{-3} mole/liter; (●) [$(NH_4)_2S_2O_8$] = 8.35 × 10^{-3} mole/liter; (△) [$(NH_4)_2S_2O_8$] = 12.52 × 10^{-3} mole/liter; (ȯ) [$(NH_4)_2S_2O_8$] = 16.69 × 10^{-3} mole/liter. [MAA] = 1.0 × 10^{-1} mole/liter; [TLA] = 5.36 × 10^{-3} mole/liter; 35 ± 0.2°C.

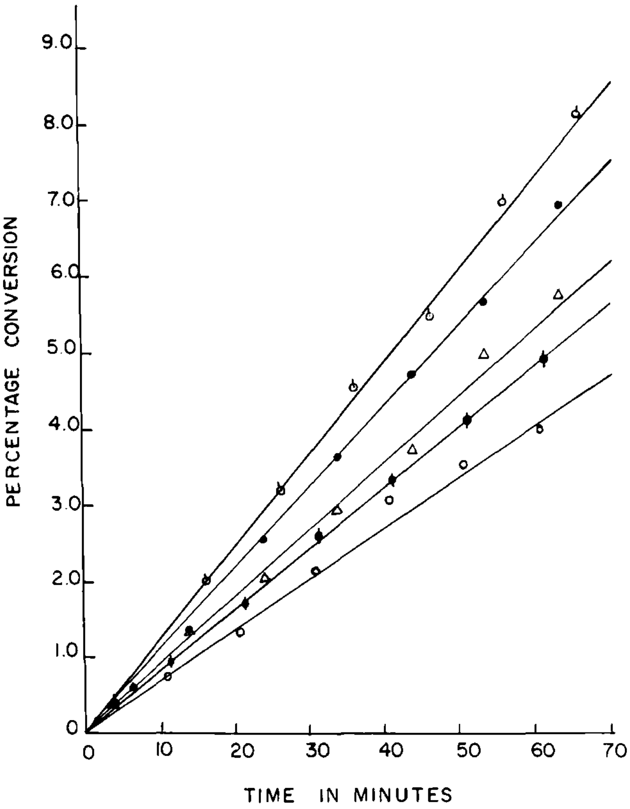

FIG. 2. Plot of initial course of polymerization for various initial concentrations of thiolactic acid: (○) [TLA] = 0.54 × 10^{-3} mole/liter; (ϕ) [TLA] = 1.07 × 10^{-3} mole/liter; (△) [TLA] = 2.14 × 10^{-3} mole/liter; (●) [TLA] = 4.29 × 10^{-3} mole/liter; (ȯ) [TLA] = 8.58 × 10^{-3} mole/liter. [MAA] = 1.0 × 10^{-1} mole/liter; [$(NH_4)_2S_2O_8$] = 4.18 × 10^{-3} mole/liter; 35 ± 0.2°C.

reported for methacrylamide polymerization initiated by persulfate alone [8] indicates that thiolactic acid is basically responsible for the higher value of monomer exponent observed in the present study. The sulfydryl radical derived from thiolactic acid may undergo coupling reaction.

$$2\,R\dot{S} \longrightarrow (RS)_2 \qquad (6)$$

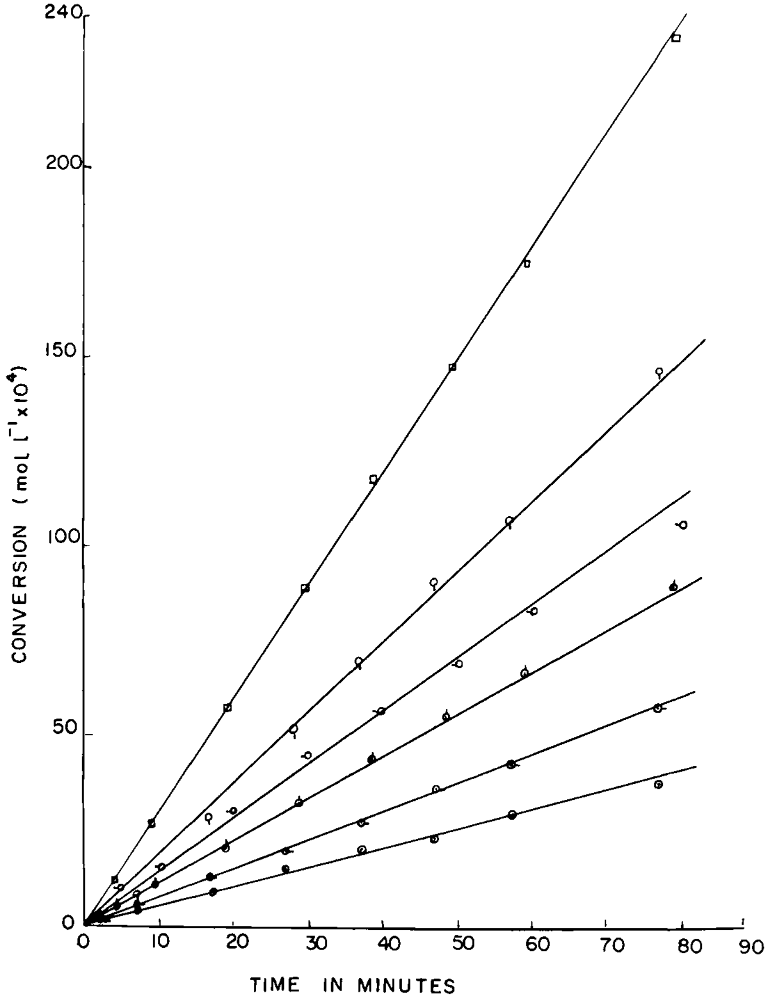

FIG. 3. Plot of initial course of polymerization for various initial concentrations of monomer: (⊙) $[MAA] = 5.0 \times 10^{-2}$ mole/liter; (⊙-) $[MAA] = 7.5 \times 10^{-2}$ mole/liter; (ȯ) $[MAA] = 10.0 \times 10^{-2}$ mole/liter; (-o) $[MAA] = 12.5 \times 10^{-2}$ mole/liter; (♀) $[MAA] = 15.0 \times 10^{-2}$ mole/liter; (□) $[MAA] = 20.0 \times 10^{-2}$ mole/liter. $[(NH_4)_2S_2O_8] = 4.18 \times 10^{-3}$ mole/liter; $[TLA] = 2.68 \times 10^{-3}$ mole/liter; 35 ± 0.2°C.

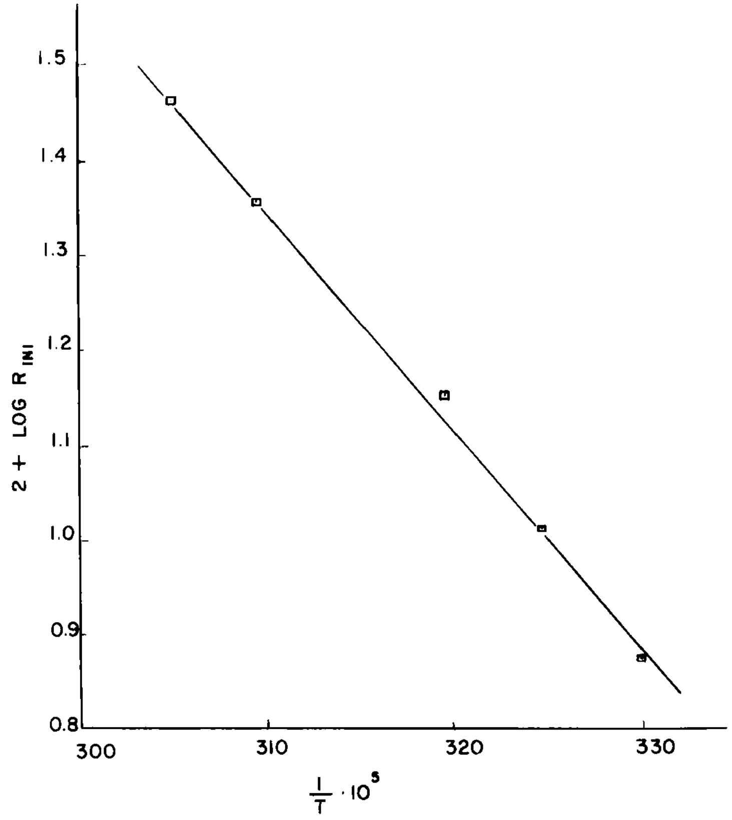

FIG. 4. Arrhenius plot. [MAA] = 5.0×10^{-2} mole/liter; [TLA] = 2.68×10^{-3} mole/liter; [$(NH_4)_2S_2O_8$] = 4.18×10^{-3} mole/liter.

Some of the primary radicals are thus lost by dimerization. As the concentration of monomer increases, the fraction of primary radicals consumed in reaction (6) decreases due to the increase in the availability of monomer. This results in an increase in the efficiency of initiation. This variation in the efficiency of initiation with monomer concentration is probably responsible for the anomalous order with respect to monomer.

The effect of temperature on the rate of polymerization was studied over the range 30-55°C. The overall activation energy calculated from the Arrhenius plot (Fig. 4) is 10.4 kcal/mole.

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