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 $35 \pm 0.1°C$ in a nitrogen atmosphere. The rate of polymerization is governed by the expression, $R_p = K[AN]$ $[S_2O_8^{2-}]^x[TMA]^{0.40}$, 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 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 α-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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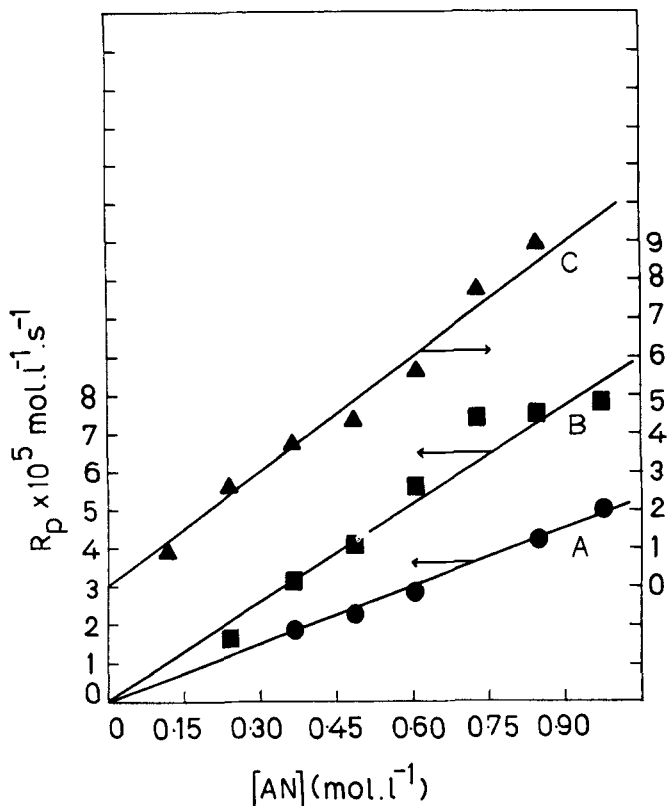*Present address: R&D, Hindusthan Photo Films, Ootacamund 643005, India.

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 5.0×10^{-3},
1.0×10^{-2}, and 1.5×10^{-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 per-
oxydisulfate concentration over the range 2.0×10^{-3} to 2.0×10^{-2}
mol/L at different concentrations of acrylonitrile. The initiator ex-
ponent was found to be 0.60 at the monomer concentration 0.3036
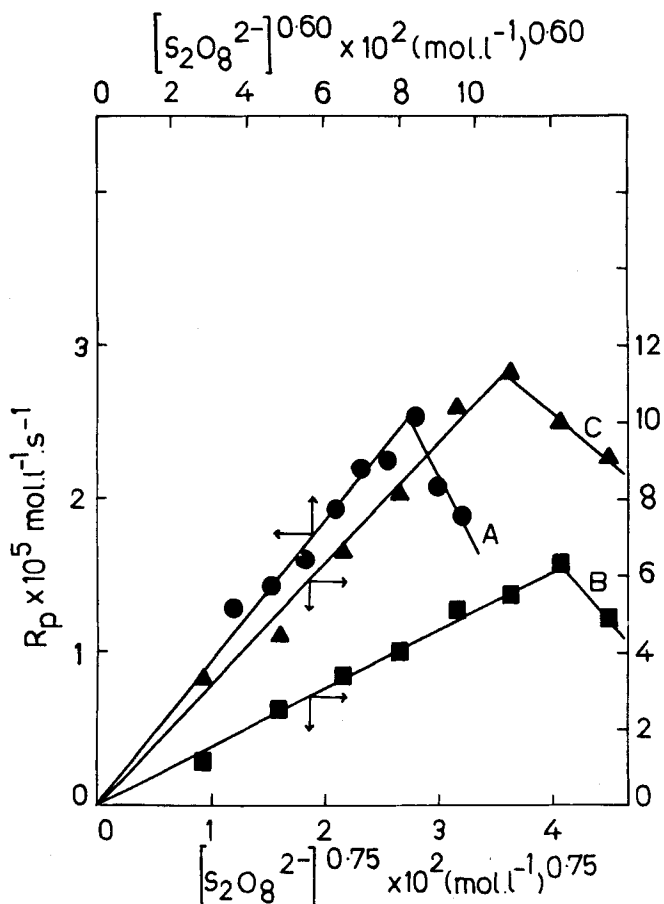mol/L (Fig. 2, Plot A), and 0.75 at higher monomer concentrations

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 concen-
trations of peroxydisulfate of 1.6×10^{-2}, 1.4×10^{-2}, and 1.2×10^{-2}
mol/L, respectively, after which the rate of polymerization shows a
decreasing trend. Generally, a negative trend in the rate with re-
spect to the initiator indicates its participation in termination reac-
tions. 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 con-
centration of peroxydisulfate led to incipient coagulation, which in
turn brought down the number of polymer particles, thereby affect-
ing the rate of polymerization.

The deviation to a slightly higher order (0.60 and 0.75) with re-
spect to the initiator concentration is indicative of mixed termination,
linear and quadratic, with the latter predominating [3]. A slight in-
crease in the order with respect to the initiator is due to change in
density of polymer particles in the reaction mixture. The contribu-
tion of the thermal homolysis of peroxydisulfate to the production of
$SO_4^{\cdot-}$ is assumed to be negligible (Eq. 1), since it would require an

activation energy higher than that observed for the overall polymer-
ization (7.3 kcal/mol). The sulfhydryl radical derived from thiomalic
acid is assumed to be the predominant initiating species. We suggest
a plausible mechanism of initiation.

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot-}. \tag{1}$$

$$S_2O_8^{2-} + RSH \longrightarrow SO_4^{\cdot-} + RS^{\cdot} + HSO_4^{-}. \tag{2}$$

$$SO_4^{\cdot-} + RSH \longrightarrow RS^{\cdot} + HSO_4^{-}. \tag{3}$$

$$RS^{\cdot} + M \longrightarrow RSM^{\cdot}. \tag{4}$$
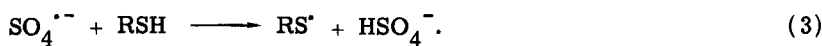
The plots of R_p vs $[TMA]^{0.40}$ are linear (Fig. 3), indicating 0.40-
order dependence on TMA concentration in the range 2.0×10^{-3} to
1.6×10^{-2} mol/L of TMA. Because TMA is a tribasic acid [8], it
dissociates to release protons in solution, which in turn catalyzes
the conversion of peroxydisulfate into HSO_4^{-}, 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 calcu-
lated to be 7.3 kcal/mol. The addition of inorganic electrolytes, such
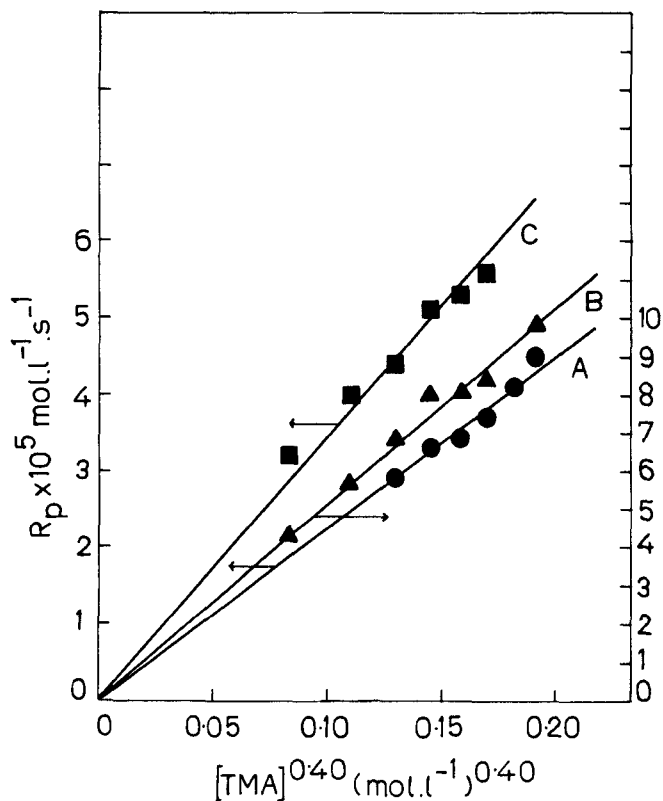as NaCl, KCl, Na_2SO_4, and $MgSO_4$, lowered the rate of polymeriza-

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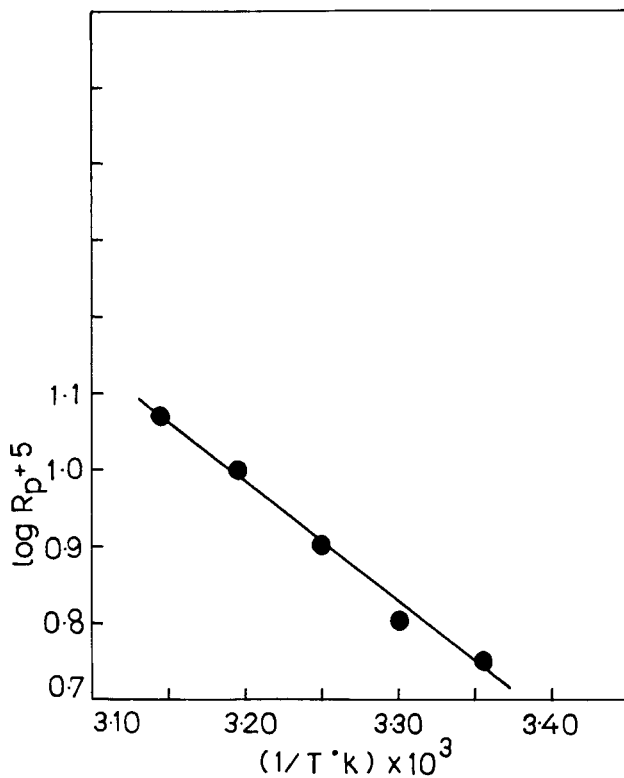
FIG. 4. Arrhenius plot of log R_p vs 1/T.

ACKNOWLEDGMENT

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