

## NOTE

**Redox Polymerization of Acrylonitrile Initiated by the System Tris Trinitratocerium(IV) Paraperiodate-propane-1,2-diol**

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The polymerization of acrylonitrile (M) initiated by the tris trinitratocerium(IV) paraperiodate-propane-1,2-diol (R) redox system has been studied in aqueous sulphuric acid under nitrogen in the temperature range 30–40°C. The relation between the rate of polymerization and  $[M]^2$  or  $[R]$  is linear.

**Key Words:** Redox, polymerization, acrylonitrile.

Several reports<sup>1–3</sup> have appeared on the mechanism and kinetics of polymerization involving ceric ion-alcohol redox system. Katai *et al.*<sup>4</sup> reported that the radical generating step in this system is not generally straight forward; for this reason and also for possible application of the system to the synthesis of graft copolymer of polysaccharide materials, the present study was undertaken.

In this paper the polymerization of acrylonitrile by a new redox system {tris trinitratocerium(IV) paraperiodate-propane-1,2-diol<sup>5–8</sup>,  $[(NO_3)_3Ce]_3 \cdot H_2IO_6$ -propane-1,2-diol} has been studied.

Acrylonitrile was purified by the method of Bamford *et al.*<sup>9</sup>. Sulphuric acid and propane-1,2-diol were Merck G.R. varieties. Doubly distilled water was used for preparation of solutions.

**Polymerization:** Appropriate quantities of the monomer and propane-1,2-diol in sulphuric acid were taken in a reaction vessel fitted with an inlet and outlet tube for nitrogen and kept in a thermostat. The mixture was deaerated for about 15 to 20 min; then the solution of  $[(NO_3)_3Ce]_3 \cdot H_2IO_6$ -propane-1,2-diol in sulphuric acid was added. The polymerization started immediately without any induction period. After a specified time interval, the reaction was arrested by addition of known excess of ferrous ammonium sulphate solution. The polymer was filtered off, washed with water and dried to constant weight. The rate of polymerization (monomer disappearance) was calculated from the slope of the plot of yield vs. time.

The relation between the conversion and reaction time for the polymerization of acrylonitrile initiated by  $[(NO_3)_3Ce]_3 \cdot H_2IO_6$ -propane-1,2-diol system is shown in Fig. 1. A limiting conversion is attained within 70 min. The percentage of conversion has also been studied at different concentrations of the substrate

(propane-1,2-diol); it increases with increase of propane-1,2-diol concentration as expected.

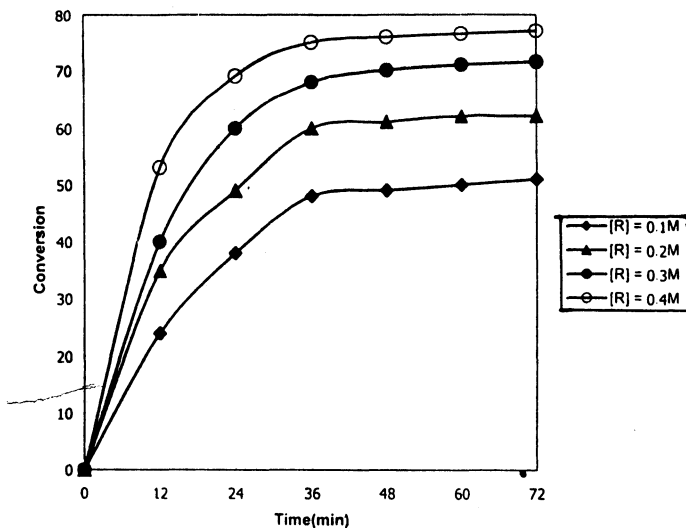


Fig. 1. Variation of rate of conversion with time  $[M] = 0.75 \text{ M}$ ;  $[\text{H}_2\text{SO}_4] = 0.9 \text{ M}$ ;  $[\text{TTCP}] = 0.005 \text{ M}$ ;  $\text{Temp.} = 35^\circ\text{C}$

The rate of polymerisation ( $R_p$ ) increased with increasing the monomer concentration (0.2–1.4 M). The plots of  $R_p$  vs.  $[M]^2$  were linear and passed through the origin (Fig. 2), hence the order with respect to  $[M]$  was 2.

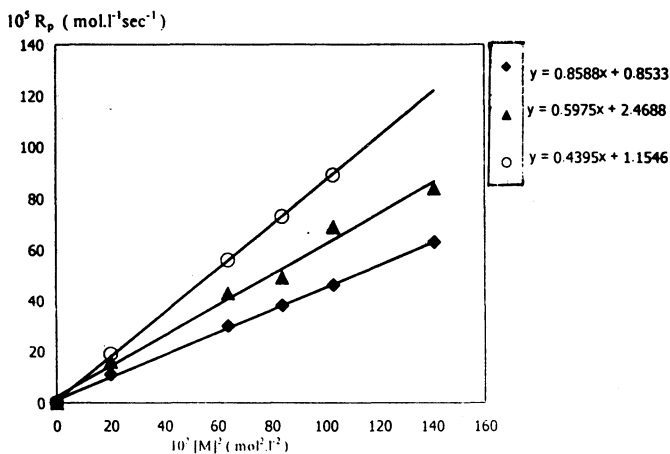


Fig. 2. Variation of rate of polymerization ( $R_p$ ) of acrylonitrile  $[M]$  with  $[M]^2$  at  $[\text{H}_2\text{SO}_4] = 0.9 \text{ M}$ ;  $[\text{TTCP}] = 0.005 \text{ M}$ ;  $[R] = 0.2 \text{ M}$ : at  $30^\circ$ ,  $35^\circ$  and  $40^\circ\text{C}$

The rate of polymerisation was also increased with increase in temperature (30–40°C) and with increasing the substrate (propane-1,2-diol) concentration in

the low concentration range (0.1–0.5 mol L<sup>-1</sup>); at higher concentrations deviation from this became apparent. The initial dependence of  $R_p$  on  $[R]$  may be understood in terms of linear termination by tris-trinitratocerium(IV) para-periodate (Fig. 3).

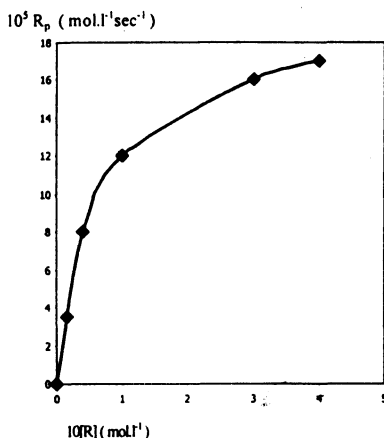


Fig. 3. Variation of rate of polymerization ( $R_p$ ) with the propane-diol concentration  $[R]$  at  $[H_2SO_4] = 0.9$  M;  $[M] = 0.8$  M;  $[TTCP] = 0.005$  M at 35°C

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