

# Micellar Effect on the Polymerization. III.\* Kinetics of Polymerization of Acrylonitrile Initiated by Ce(IV)–Glucose System in Presence of Cationic Micelles

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## SYNOPSIS

The micellar effect on the kinetics of ceric ion-initiated polymerization of acrylonitrile (AN) in the presence of glucose was studied in the temperature range 40–50°C. The effects of concentration of the metal ion, monomer, sulfuric acid, substrate (glucose), emulsifier, some inorganic salt, and organic solvent on the rate of polymerization ( $R_p$ ) were also investigated. The remarkable features of the investigation involve the enhancement of  $R_p$  in the presence of a micelle, the derivation of the rate expression for the above system along with the calculation of activation energy, and prediction of optimum conditions. Comparison of the rates for a micellar medium with those for the aqueous medium indicates that cationic micelles exert an accelerating influence on the rates of polymerization. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The rates of many chemical reactions are affected by incorporating the reactants into their micellar pseudophase.<sup>1</sup> Barton et al.<sup>2,3</sup> showed that the anion-active emulsifier affects the relative molecular mass of polyacrylamide and polymethacrylamide, but that it showed no effect on the polymerization rate. Kim<sup>4</sup> observed an increase of the rate of polymerization of acrylamide initiated by sodium hydrogen trioxosulfate at concentrations of the emulsifier higher than its critical micellar concentration. Shukla and Mishra<sup>5</sup> found that the rate of polymerization of acrylamide in water initiated by the potassium permanganate/ascorbic acid system increases only at concentrations higher than the CMC of the applied anion-active emulsifier, but was not affected below the CMC value. The nonionic emulsifier  $\alpha$ -hydro-*w*-(-4-isooctyl phenoxy)polyoxyethylene (triton X-100) did not affect the rate, whereas the cation-ac-

tive emulsifier NCTAB and cetyl pyridinium bromide decreased the polymerization rate.<sup>5</sup> A redox system as the initiator for acrylonitrile (AN) polymerization in the presence of the surfactant NCTAB was used by Baxendale et al.,<sup>6</sup> but Lind et al.<sup>7</sup> used potassium lauryl sulfate as the emulsifier with potassium persulfate as the initiator. Though the rate of polymerization is increased in both the cases, in the case of the redox initiator, the enhancement was remarkable. The present article reveals the influence of a surfactant on Ce(IV)–glucose-initiated polymerization of AN.

## EXPERIMENTAL

### Materials

Acrylonitrile (AN) was washed with 5% NaOH, 3% orthophosphoric acid, followed by repeated washing with conductivity water, and dried over fused calcium chloride. Then, it was distilled in an atmosphere of nitrogen and, finally, stored in a refrigerator for use. Reagents like ceric ammonium sulfate, glucose, ferrous ammonium sulfate, *N*-cetyltrimethylammonium bromide (emulsifier), and sulfuric acid (18M) were all of AnalaR grade and

\* Part 1: H. K. Das and B. C. Singh, *J. Appl. Polym. Sci.*, **49**, 1107–1113 (1993). Part 2: C. M. Patra and B. C. Singh, *J. Appl. Polym. Sci.*, **52**, 1549–1556 (1994).

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Journal of Applied Polymer Science, Vol. 58, 1999–2003 (1995)  
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were used as such: a *N*-cetyltrimethylammonium bromide (NCTAB) was purified according to the method of Dynstee and Grunwald. Conductivity water was prepared by redistilling distilled water over alkaline  $\text{KMnO}_4$  in an all-glass Pyrex unit.

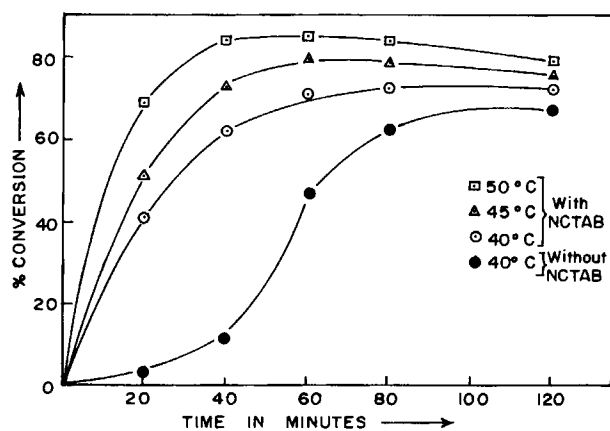
### Polymerization

Appropriate quantities of monomer, glucose, emulsifier (NCTAB), and sulfuric acid were mixed in the reaction vessel (a Pyrex vessel fitted with a  $\text{B}_{24/29}$  socket, carrying a  $\text{B}_{24/29}$  cone with inlet and outlet tubes) and thermostated at the desired temperature with an accuracy of  $\pm 0.1^\circ\text{C}$ . A required amount of ceric ammonium sulfate solution (in  $1\text{ M H}_2\text{SO}_4$ ) was added and the time was noted. After the specified time interval, the polymerization was arrested by adding an excess of ferrous ammonium sulfate solution. The polymer formed was filtered off, washed repeatedly with conductivity water, and dried to a constant weight. The rate of polymerization ( $R_p$ ) and the percentage conversion were calculated by using the following formula:

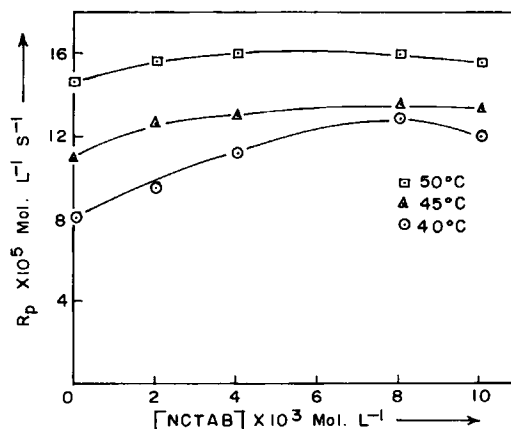
$$\text{Rate of polymerization } (R_p) = \frac{1000 \times W}{V \times t \times M}$$

where  $W$  is the weight of polymer;  $V$ , the volume of reaction mixture in milliliters (20 mL here);  $t$ , the time in seconds; and  $M$ , the molecular mass of the monomer (for AN,  $M = 53.06$ ):

$$\% \text{ Conversion} = \frac{\text{wt of polymer}}{\text{wt of monomer}} \times 100$$



**Figure 1** Time conversion curves:  $[\text{AN}] = 0.759 \text{ mol L}^{-1}$ ;  $[\text{Ce(IV)}] = 0.025 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol L}^{-1}$ ;  $[\text{glucose}] = 0.0025 \text{ mol L}^{-1}$ ;  $[\text{NCTAB}] = 0.005 \text{ mol L}^{-1}$ .



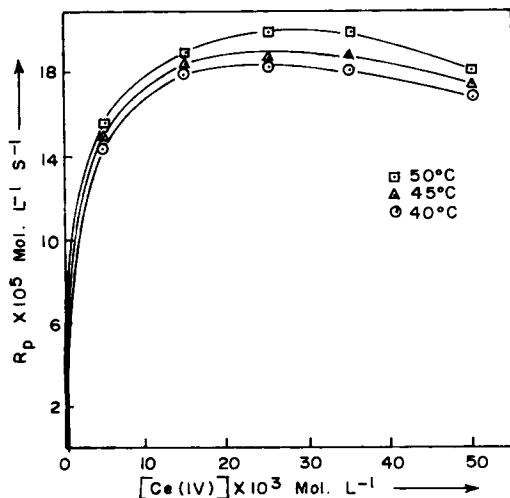
**Figure 2**  $R_p$  vs.  $[\text{NCTAB}]$  plots:  $[\text{AN}] = 0.759 \text{ mol L}^{-1}$ ;  $[\text{Ce(IV)}] = 0.015 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol L}^{-1}$ ;  $[\text{glucose}] = 0.0025 \text{ mol L}^{-1}$ ; time = 1 h.

### RESULTS AND DISCUSSION

The effect of time on percentage conversion was studied both in the presence and absence of a cationic emulsifier (NCTAB) at a temperature range  $40\text{--}50^\circ\text{C}$ . It is reflected in Figure 1. The percentage conversion was found to be higher for systems having an emulsifier than that in its absence. A limiting conversion was attained within 60 min. However, after 1 h, the increase in percentage conversion was observed to be negligible. This may be due to the creation of a biphasic system (bulk phase and micellar pseudophase) beyond its CMC in aqueous medium.<sup>8</sup>

During the course of AN polymerization at different concentrations of the emulsifier (NCTAB) ranging from  $0.002$  to  $0.01 \text{ mol L}^{-1}$ , it is clearly revealed that the polymerization rate is enhanced up to  $0.008 \text{ mol L}^{-1}$  and then it decreases (Fig. 2). The concentration of emulsifier at which the  $R_p$  is maximum represents the CMC. The increasing trend of  $R_p$  with soap concentration is due to the emulsifying effect of soap on monomer-polymer particles. The decrease in the  $R_p$  value may be due to the fast rate of mutual termination by the growing macroradicals initiated in the interior of the soap micelle at higher emulsifier concentration. This fact is in close agreement with the reports of Fendler and Fendler<sup>1</sup> and of Baxendale et al.<sup>6</sup>

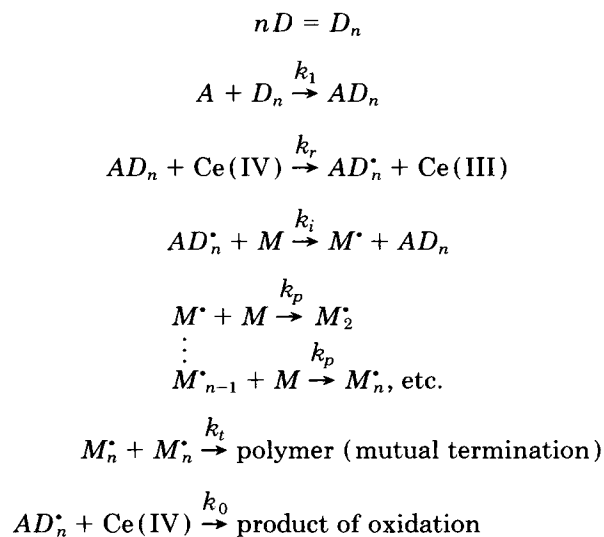
Figure 3 represents the effect of variation of  $\text{Ce(IV)}$  concentration at three different temperatures ( $40$ ,  $45$ , and  $50^\circ\text{C}$ ) on the rate of polymerization. The rate of polymerization increases by increasing the concentration of  $\text{Ce(IV)}$  from  $0.005\text{--}0.025 \text{ mol L}^{-1}$  and then it decreases slightly. This



**Figure 3**  $R_p$  vs.  $[Ce(IV)]$  plots:  $[AN] = 0.759 \text{ mol L}^{-1}$ ;  $[glucose] = 0.0025 \text{ mol L}^{-1}$ ;  $[H_2SO_4] = 0.5 \text{ mol L}^{-1}$ ;  $[NCTAB] = 0.005 \text{ mol L}^{-1}$ ; time = 1 h.

clearly invokes the prevalence of mutual termination over the linear one<sup>8</sup> at lower concentrations of  $Ce(IV)$ .

Based on these facts, it is proposed that the polymerization process occurs in the micellar phase in the presence of a surfactant. A free-radical mechanism is assumed in the present system as reported by Harkins<sup>9</sup> for emulsion polymerization. In the micellar phase, we may suggest the following equilibria:



where  $D$  = detergent,  $D_n$  = micelle,  $A$  = organic substrate (glucose), and  $M$  = monomer (AN).

With the usual steady-state assumption, the following expression for the rate of polymerization may be deduced:

$$\begin{aligned}
 \frac{d[AD_n^*]}{dt} &= k_1 k_r [A][D_n][Ce(IV)] \\
 &\quad - k_i [M][AD_n^*] - k_0 [AD_n^*][Ce(IV)] = 0
 \end{aligned}$$

$$\frac{d[M_n^*]}{dt} = k_i [AD_n^*][M] - k_t [M_n^*]^2 = 0$$

$$\begin{aligned}
 R_p &= k_p [M_n^*][M] \\
 &= k_p \left\{ \frac{k_1 k_i k_r [A][D_n][Ce(IV)][M]}{k_i k_t [M] + k_0 k_t [Ce(IV)]} \right\}^{1/2} \times [M]
 \end{aligned}$$

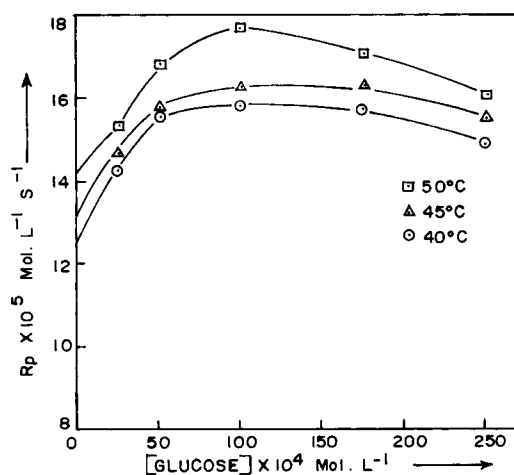
or

$$R_p = k_p \left\{ \frac{k_1 k_i k_r [A][D_n][Ce(IV)]}{k_i k_t [M] + k_0 k_t [Ce(IV)]} \right\}^{1/2} \times [M]^{3/2}$$

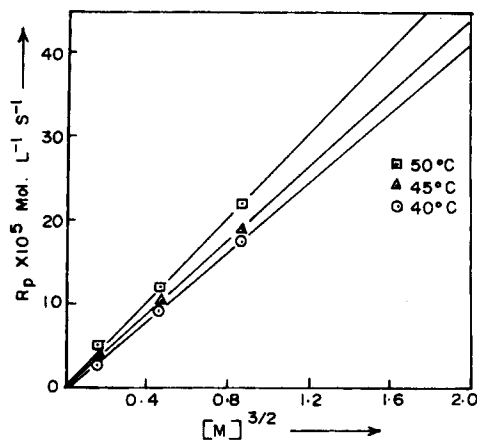
where  $Ce(IV)$ ,  $R_p$ ,  $k_1$ ,  $k_r$ ,  $k_i$ ,  $k_p$ ,  $k_t$ , and  $k_0$  are the ceric ion, rate of polymerization, and different rate constants, respectively.

The effect of variation of glucose concentration on the rate of polymerization at three different temperatures, 40, 45, and 50°C, is shown in Figure 4. The rate of polymerization increases with increasing concentration of glucose up to 0.01 mol L<sup>-1</sup> and then it decreases. A similar observation was made by Sinha et al.<sup>10</sup>

The effect of monomer concentration on the rate has been studied at three different temperatures, 40, 45, and 50°C (Fig. 5). It is observed that the rate of polymerization increases with increase in monomer concentration. The higher rate of polymerization is attributed to the presence of a greater number of polymer-monomer particles in the micellar sys-



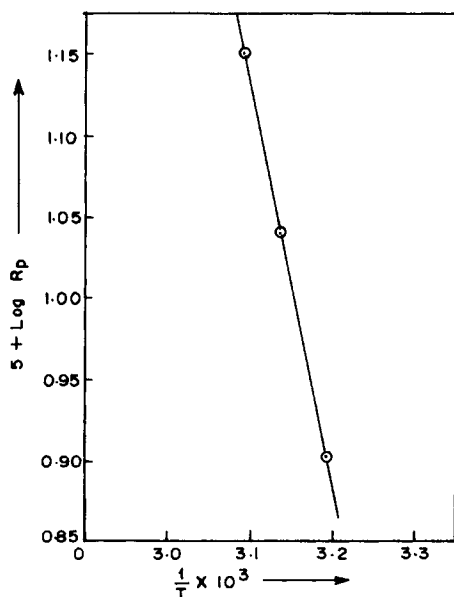
**Figure 4**  $R_p$  vs.  $[glucose]$  plots:  $[AN] = 0.759 \text{ mol L}^{-1}$ ;  $[Ce(IV)] = 0.015 \text{ mol L}^{-1}$ ;  $[H_2SO_4] = 0.25 \text{ mol L}^{-1}$ ;  $[NCTAB] = 0.008 \text{ mol L}^{-1}$ ; time = 1 h.



**Figure 5**  $R_p$  vs.  $[M]^{3/2}$  plots:  $[Ce(IV)] = 0.015 \text{ mol L}^{-1}$ ;  $[\text{glucose}] = 0.01 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol L}^{-1}$ ;  $[\text{NCTAB}] = 0.008 \text{ mol L}^{-1}$ ; time = 1 h.

tem.<sup>11</sup>  $R_p$  was found to be proportional to  $[M]^{3/2}$ . The plot of  $R_p$  vs.  $[M]^{3/2}$  is a straight line passing through the origin. However, deviation occurs at much higher concentration of the monomer.<sup>12</sup> This is probably due to the complex nature of the kinetics applied to polymeric systems.

The rate of polymerization increases with increase in temperature. A sample Arrhenius plot of  $\log R_p$  vs.  $1/T$  (Fig. 6) reveals that the overall energy of activation of such a polymerization reaction is 9.212 kcal/mol.



**Figure 6** Arrhenius plot:  $[\text{AN}] = 0.759 \text{ mol L}^{-1}$ ;  $[Ce(IV)] = 0.015 \text{ mol L}^{-1}$ ;  $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol L}^{-1}$ ;  $[\text{glucose}] = 0.0025 \text{ mol L}^{-1}$ ;  $[\text{NCTAB}] = \text{nil}$ ; time = 1 h; temperatures = 40, 45, and 50°C.

**Table I** Effect of Concentration of Acid on Percentage Conversion:  $[\text{AN}] = 0.759 \text{ Mol L}^{-1}$ ,  $[Ce(IV)] = 0.015 \text{ Mol L}^{-1}$ ,  $[\text{Glucose}] = 0.0025 \text{ Mol L}^{-1}$ ,  $[\text{NCTAB}] = 0.005 \text{ Mol L}^{-1}$ , Time = 1 h

$[\text{H}_2\text{SO}_4]$	Temp 40°C (% Conv.)	Temp 45°C (% Conv.)	Temp 50°C (% Conv.)
0.15	62.48	73.08	78.27
0.25	67.52	77.54	78.16
0.35	69.15	78.39	79.23
0.45	73.50	78.96	80.44
0.60	57.91	73.84	75.45

The effect of sulfuric acid concentration on the rate of polymerization was studied at three different temperatures, 40, 45, and 50°C, in the concentration range of 0.15–0.6 mol L<sup>-1</sup>. The rate of polymerization keeps increasing with increasing concentration of acid up to 0.45 mol L<sup>-1</sup>, and then decreases (Table I). The increasing trend may be due to the formation of a greater number of effective Ce(IV) species with increasing concentration of the acid, but at higher acid concentration, the effective species are limited.

The effect of different categories of cosolvents on the rate of polymerization is reflected in Table II. The decreasing order of  $R_p$  in the presence of different cosolvents is as follows:

DMF > control > acetone

> ethyl alcohol > benzene

DMF increases the  $R_p$  value slightly, whereas benzene retards it. This fact is in agreement with that reported by Ionescu et al.<sup>13</sup>

The effect of salts on  $R_p$  as depicted in Table II follows the decreasing order given below:

NaCl > control > KCl > MnCO<sub>3</sub> > CuSO<sub>4</sub>

KCl, MnCO<sub>3</sub>, and CuSO<sub>4</sub> retard the rate of polymerization, whereas NaCl enhances the rate of polymerization slightly producing a negligible effect. The maximum depression of  $R_p$  in case of CuSO<sub>4</sub> may probably be due to the dissociation of added salt which interferes with the normal polymerization process, resulting in the premature termination of the growing polymer chain.<sup>12,14,15</sup>

## CONCLUDING REMARKS

In conclusion, it should be noted that although our results are very similar to the results reported earlier

**Table II Effect of Solvent and Salt on Percentage Conversion: [AN] = 0.759 Mol L<sup>-1</sup>, [Ce(IV)] = 0.015 Mol L<sup>-1</sup>, [Glucose] = 0.01 Mol L<sup>-1</sup>, [NCTAB] = 0.008 Mol L<sup>-1</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 0.25 Mol L<sup>-1</sup>, Time = 1 h, Temp = 45°C**

Name of Solvent	% Conversion	Name of Inorganic Salt	Conversion
Control	77.41	Control	75.76
Benzene	45.40	NaCl	79.91
Acetone	76.44	CuSO <sub>4</sub>	7.85
Ethyl alcohol	65.22	MnCO <sub>3</sub>	42.90
DMF	77.44	KCl	69.82

by us there is one remarkable feature. The optimum concentration of sulfuric acid has been found to be 0.45 mol L<sup>-1</sup>, which is lower than the concentration of sulfuric acid after which maximum yield was found by Patra and Singh<sup>16</sup>:

[Ce(IV)] 0.035 mol L<sup>-1</sup>; [NCTAB] 0.008 mol L<sup>-1</sup>;

[Glucose] 0.01 mol L<sup>-1</sup>; [H<sub>2</sub>SO<sub>4</sub>] 0.45 mol L<sup>-1</sup>

One of us (A. P.) is grateful to U.G.C., New Delhi, for a junior research fellowship.

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Received October 18, 1994

Accepted February 25, 1995