Effect of Organized Anionic Surfactant System on Kinetics of Polymerization of Acrylonitrile Initiated by Ce(IV): Citric Acid and Other Organic Substrates

M. PATRA, A. K. PANIGRAHI, and B. K. SINHA*

Post Graduate Department of Chemistry, Sambalpur University, Jyoti Vihar, Burla 768019, Orissa, India

SYNOPSIS

The polymerization of acrylonitrile (AN) using the Ce(IV)–citric acid (CA) redox system as an initiator in aqueous nitric acid solution, in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS), has been kinetically studied at a temperature range of 25–45°C. The rate of polymerization (R_p) and disappearance of Ce(IV) ($-R_{Ce}$) increase with increasing concentration of SDS, above its critical micelle concentration (cmc), when the surfactant molecules are organized. R_p was found to be proportional to $[AN]^{1.5}$ and $[CA]^{0.5}$. With other organic substrates, R_p follows the increasing order of sorbitol $\geq$ mannitol $>$ glycerol $>$ CA. But it was found to decrease considerably in the presence of cationic surfactant (CTAB), and nonionic surfactant (Triton-X-100) had no effect on the rate. $-R_{Ce}$ varies linearly with [Ce(IV)] and [CA]. Both R_p and $-R_{Ce}$ increase with increasing temperature. The overall activation energy was found to be 18.31 and 13.72 kcal/mol in the absence and presence of 0.015M SDS, respectively. The chain length of the polyacrylonitrile has also increased with increasing SDS concentration. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A considerable amount of work has been done on the kinetics of polymerization of vinyl monomers using different redox systems. Various workers[1-7] have vividly studied vinyl polymerization initiated by a redox system with Ce(IV). A review of the literature reveals that the polymerization of vinyl monomers has been studied in the micellar phase,[8-13] emulsions,[14-19] inverse emulsions,[20,21] and microemulsion media[22] using various redox systems as initiator. The present work deals with the kinetics of polymerization of acylonitrile in the micellar aggregates of SDS mainly using Ce(IV)–citric acid as the redox system.

EXPERIMENTAL

Materials

Acrylonitrile (AN) (Sisco Chemical) was purified by washing with 5% NaOH, 3% Ortho phosphoric acid, and finally with triply distilled water and distilling under reduced pressure. Sodium dodecyl sulfate (SDS) [(British Drug House sample)] was recrystallized from absolute alcohol and methanol sequentially. Ceric ammonium nitrate, citric acid (CA), sodium nitrate, and nitric acid were analar-grade chemicals and were used as such, without further purification. Solutions for the study were prepared with triply distilled water free from oxygen. The nitrogen gas, used for deaeration, was made free from oxygen and other impurities by passing through several columns of Fieser's solution, a column of saturated solution of lead acetate, and finally through a bottle containing triply distilled water.

Method of Polymerization

The polymerization was carried out in a Pyrex tube of 150 mL capacity, which was sealed at the bottom and fitted at the top with a standard joint stopper that had inlet and outlet tubes for passing of nitrogen and a microburette fitted vertically to the stopper. The aqueous solution of AN, CA, HNO₃, NaNO₃ (to maintain proper ionic strength), and SDS in appro-
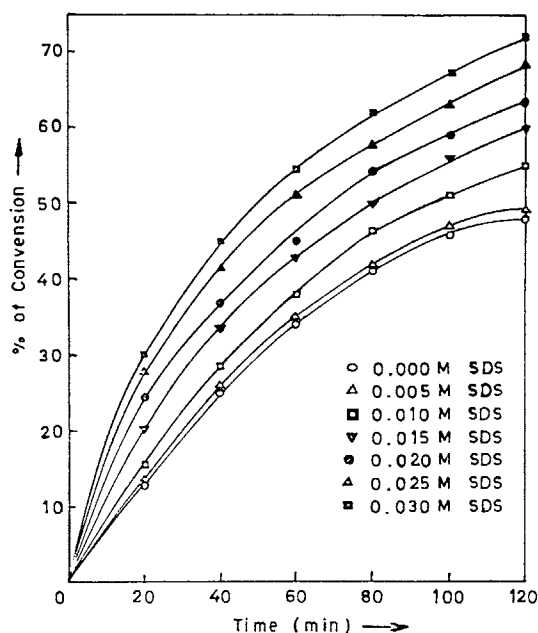

Figure 1 Effect of SDS concentration on percent of conversion. [AN] = $0.694M$; [CA] = $0.108M$; [Ce(IV)] = $5.01 \times 10^{-3}M$; [H$^+$] = $0.495M$; μ = $0.5M$; temperature = 35°C.

priate concentrations were taken in the reaction tube. Nitrogen gas was bubbled for about half an hour, and stop-cocks were closed. The solution was thermostated to attain the desired temperature followed by addition of ceric ammonium nitrate solution in $1M$ HNO$_3$ from the microburette. The volume of the reaction mixture was adjusted to 20 mL. The appearance of turbidity indicates starting of polymerization. After a definite 20 min, the reaction was quenched by 2 mL of $0.01M$ excess standard ferrous ammonium sulfate solution. The polymer so obtained was filtered off through a G$_4$ crucible and kept at 50–60°C until a constant weight was attained. The filtrate was analyzed for residual Ce(IV) by cerimetry using ferroin as an indicator.

Intrinsic Viscosity

The intrinsic viscosity was measured by a suspended level Ubblehode viscometer at 30°C, using Huggin's and Kramer's relationship.[23]

RESULT AND DISCUSSION

Effect of Surfactant

The interesting observations in this polymerization in the presence of an anionic surfactant are as follows:

1. An increase of the rate of polymerization with an increase in surfactant (SDS) concentration
2. An increase of the percentage conversion of monomer with an increase in the SDS concentration
3. A change of nature (i.e., chain length) of the polymer in the presence of SDS.

In aqueous medium, above the critical micelle concentration (cmc), the surfactant molecules become aggregated to form micelles.[24] The vinyl monomer (AN) and organic substrate (CA) are solubilized in the micellar core of SDS, due to the hydrophobic interaction. The concentration of Ce(IV) increased at the Stern layer of the anionic micellar due to electrostatic attraction, as a result of which the rate of polymerization (R_p) as well as the percentage of conversion have increased (Fig. 1). The R_p decreased considerably in the presence of cationic surfactant (CTAB) due to nonavailability of Ce(IV) at the Stern layer, which can be explained by electrostatic repulsion of Ce(IV) with the positively charged Stern layer of the CTAB micelle. This observation indicates that mostly the monomer and citric acid get solubilized in the micellar core. The solubility of acrylonitrile in water is appreciable (i.e., 7.5 g per 100 mL[25]). Hence the overall polymerization rate R_p can be assumed as the sum of the rates of polymerization in the bulk phase (R_p) and that in the micellar phase (R_p^m) (i.e., $R_{p\,(\text{obs})} = R_p + R_p^m$). But beyond cmc of the surfactant, $R_p \ll R_p^m \approx R_{p\,(\text{obs})}$. The nonionic surfactant (Triton-X-100) has no effect on the R_p. Similar types of changes were also observed by other workers.[26] The rate of Ce(IV) dis-

Table I Effect of Surfactant Concentration on R_p and $-R_{Ce}$

Surfactant (mol L^{-1})	$R_p \times 10^4$ (mol L^{-1} s^{-1})		$-R_{Ce} \times 10^7$ (mol L^{-1} s^{-1})	
	SDS	CTAB	SDS	CTAB
0.000	0.80	—	0.75	—
0.005	0.82	0.56	0.75	0.40
0.010	0.96	0.32	2.25	0.15
0.015	1.37	0.20	4.50	0.15
0.020	1.75	0.21	8.75	0.15
0.025	2.05	0.18	12.50	0.15
0.030	2.19	0.18	13.50	0.15

[AN] = $0.694M$; [CA] = $0.108M$; [Ce(IV)] = $5.01 \times 10^{-3}M$; [H$^+$] = $0.495M$; μ = $0.5M$; temperature = 35°C.
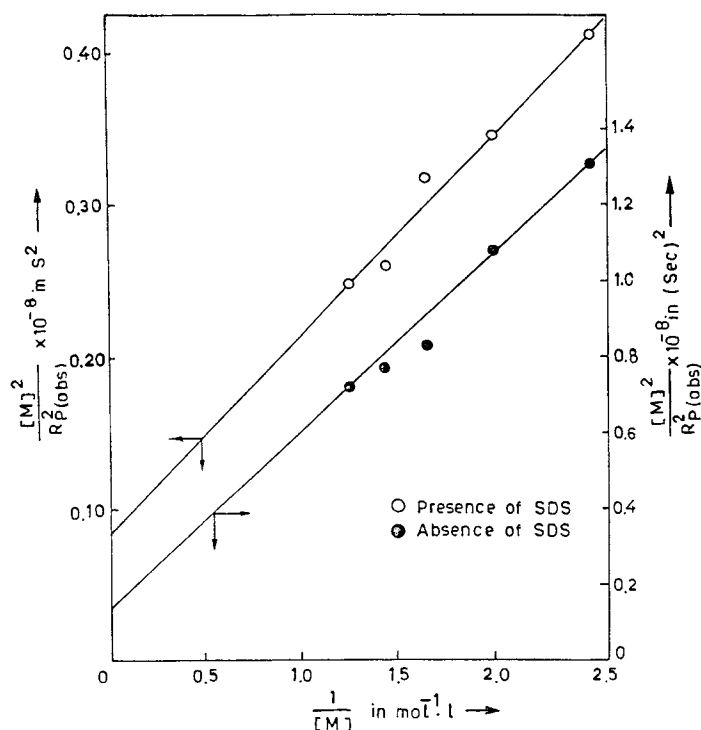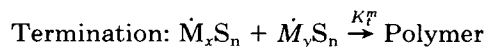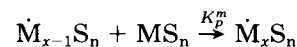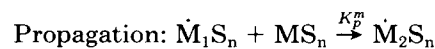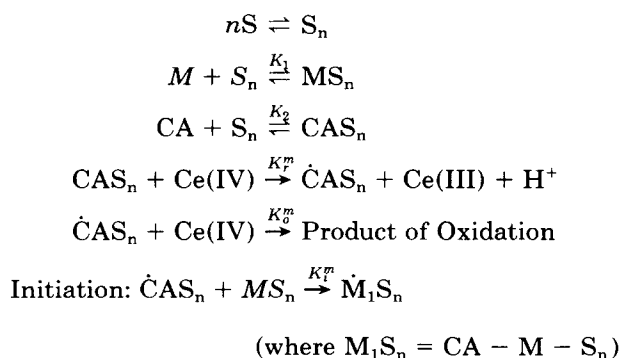
Figure 2 $[M]^2/R^2_{p\,(obs)}$ vs. $1/[M]$. $[Ce(IV)] = 5.01 \times 10^{-3}M$; $[CA] = 0.108M$; $[H^+] = 0.495M$; $\mu = 0.5M$; temperature = 35°C.

appearance $(-R_{Ce})$ has also increased with increasing $[SDS]$ (Table I).

Reaction Mechanism and Kinetic Scheme

Based on the aforementioned facts, it is concluded that the polymerization process occurs mostly in the micellar phase, in the presence of anionic surfactant (SDS), above its cmc. Hence, to explain the kinetic results, the following free radical mechanism is proposed:

$$nS \rightleftharpoons S_n$$

$$M + S_n \overset{K_1}{\rightleftharpoons} MS_n$$

$$CA + S_n \overset{K_2}{\rightleftharpoons} CAS_n$$

$$CAS_n + Ce(IV) \overset{K_i^m}{\rightarrow} \overset{\cdot}{C}AS_n + Ce(III) + H^+$$

$$\overset{\cdot}{C}AS_n + Ce(IV) \overset{K_o^m}{\rightarrow} Product\ of\ Oxidation$$

Initiation: $\overset{\cdot}{C}AS_n + MS_n \overset{K_i^m}{\rightarrow} \overset{\cdot}{M}_1S_n$

(where $M_1S_n = CA - M - S_n$)

Propagation: $\overset{\cdot}{M}_1S_n + MS_n \overset{K_p^m}{\rightarrow} \overset{\cdot}{M}_2S_n$

$$\overset{\cdot}{M}_{x-1}S_n + MS_n \overset{K_p^m}{\rightarrow} \overset{\cdot}{M}_xS_n$$

Termination: $\overset{\cdot}{M}_xS_n + \overset{\cdot}{M}_yS_n \overset{K_t^m}{\rightarrow} Polymer$

where M is the monomer; S is the surfactant; S_n is the micelles; K_1, K_2 are association constants; and K_i^m, K_p^m, K_t^m, K_o^m, and K_r^m are different rate constants.

In the preceding scheme, the possibility of linear termination is ruled out due to the absence of Ce(IV) in the polymer chain. Using steady-state assumption and mutual termination, the rate of polymerization (R_p) and the rate of Ce(IV) disappearance $(-R_{Ce})$ are expressed as

$$R_p^m = \frac{K_p^m[MS_n]^{1.5}[Ce(IV)]^{0.5}}{(K_t^m)^{0.5}}$$

$$\times \left\{ \frac{K_r^m[CAS_n]}{[MS_n] + (K_o^m/K_i^m)[Ce(IV)]} \right\}^{0.5} \quad (1)$$

$$-R_{Ce}^m = K_r^m[Ce(IV)][CAS_n] \quad (2)$$

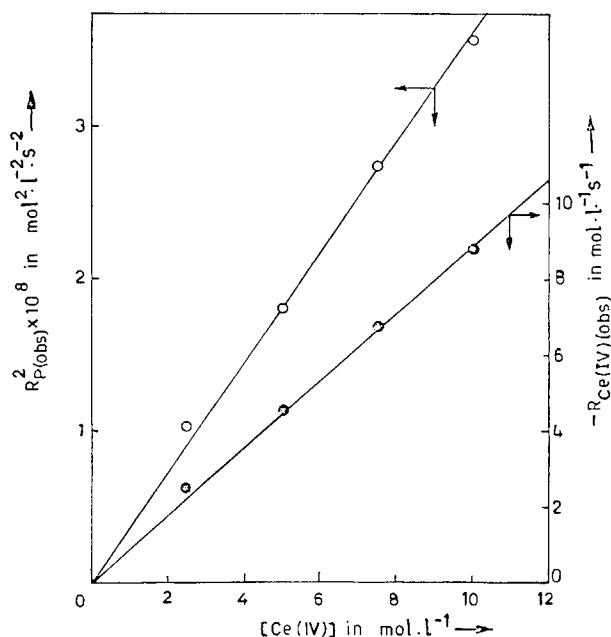On squaring eq. (1) with proper substitution and taking the reciprocal, it can be rearranged to

Figure 3 Effect of Ce(IV) concentration on rate of polymerization and rate of Ce(IV) disappearance. [AN] = 0.694M; [CA] = 0.108M; [SDS] = 0.015M; [H$^+$] = 0.495M; μ = 0.5M; temperature = 35°C.

Figure 4 Effect of organic substrate concentration on rate of polymerization. [AN] = 0.694M; [Ce(IV)] = 5.01 × 10^{-3}M; [SDS] = 0.015M; [H$^+$] = 0.495M; μ = 0.5M; temperature = 35°C.

$$\frac{[M]^2}{(R_p^m)^2} = \frac{K_t^m}{K_1^2 K_2(K_p^m)K_r^m[Ce(IV)][CA][S_n]^3}$$

$$+ \frac{K_o^m K_t^m}{K_1^3 K_2(K_p^m)K_i^m K_r^m[CA][M][S_n]^4} \quad (3)$$

Rate Parameter

From the plots of [M]^2/(R_p)^2 versus 1/[M] (Fig. 2) and [M]^2/(R_p)^2 versus 1/[Ce(IV)] (not shown), (K_o^m/$K_i^m K_1$) were calculated to be 0.358 and 0.371 mol · L^{-1}, respectively. Substituting the value of K_o/K_i that obtain from the plot of [M]^2/(R_p)^2 versus 1/[M] (Fig. 2) in absence of surfactant, K_1 was computed as 7.92 × 10^2 mol^{-1}. From the plot of $-R_{Ce(obs)}$ versus [CA] (not shown), K_r was found to be 19.96 × 10^{-3} mol^{-1} L s^{-1}. Using the values of K_r and S$_n$ in eq. (2), K_2 was found to be 0.892 × 10^4 mol^{-1} L. To calculate S$_n$, with the help of the expression [S$_n$] = (C_D − CMC)/N, the aggregation number N has been taken to be 62.[24]

Effect of Acrylonitrile Concentration

The $R_{p\,(obs)}$ was found to be proportional to 1.5 power of concentration of acrylonitrile, which was observed from the straight-line plot of $R_{p\,(obs)}$ versus [M]$^{1.5}$,
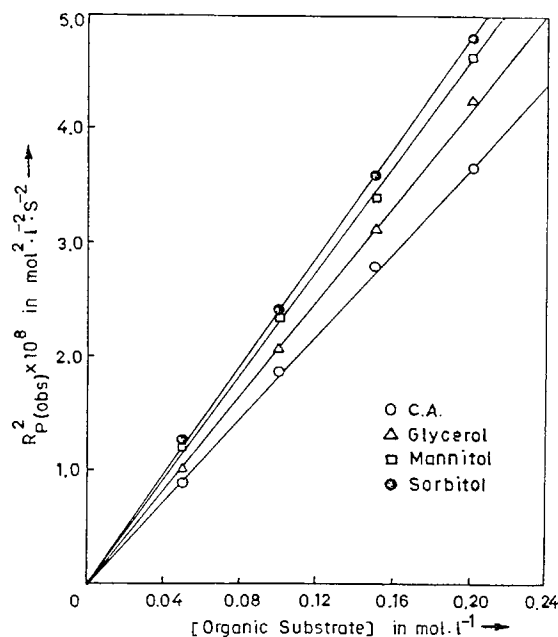
which passes through the origin. This type of result in fact supports the mutual type of termination. On increasing the concentration of acrylonitrile (0.4–0.8M), its solubilization increases in the SDS micelles, which leads to a greater number of free radical formation in the micellar media, resulting in an increase in the rate as well as percentage conversion. This fact also supports our proposed kinetic scheme and has also been observed by other workers.[1a,2,9a] The plot of [M]^2/$R_{p(obs)}^2$ versus 1/[M] is a straight line having an intercept, which explains the rate

Table II Effect of Acid Concentration on R_p and $-R_{Ce}$

[H$^+$] (mol L^{-1})	μ (mol L^{-1})	R_p × 10^4 (mol L^{-1} s^{-1})	$-R_{Ce}$ × 10^7 (mol L^{-1} s^{-1})
0.206	5.0	1.54	5.90
0.298	5.0	1.48	5.40
0.396	5.0	1.42	4.95
0.495	5.0	1.37	4.50
0.295	3.0	1.34	4.45
0.395	4.0	1.30	4.50

[SDS] = 0.015M; [AN] = 0.694M; [Ce(IV)] = 5.01 × 10^{-3}M; [CA] = 0.108M; temperature = 35°C.

Table III Effect of SDS Concentration on [η] and Chain Length

[SDS] (mol L^{-1})	[η] (g^{-1} L)	Chain Length (n)
0.000	0.71	787
0.005	0.72	894
0.010	0.99	1230
0.015	1.26	1691
0.020	1.48	2096
0.025	1.63	2384
0.030	1.73	2581

expression. The rate of disappearance of Ce(IV) also increases with increasing [AN].

Effect of [Ce(IV)]

It was observed that $R_{p(obs)}$ increases with increasing Ce(IV) concentration (2.5 × 10^{-3}–10.0 × 10^{-3}M). This can be explained by an increasing number of Ce(IV) in the Stern layer of SDS micelles due to electrostatic attraction. The plot of $R_{p(obs)}$ vs. [Ce(IV)] shows a straight line passing through the origin (Fig. 3), which is in confirmation with eq. (1). Similar findings are reported by other workers.[3,9,10] The rate of Ce(IV) disappearance was directly proportional to [Ce(IV)]. The plot of $-R_{Ce(obs)}$ vs. [Ce(IV)] (Fig. 3) is a straight line passing through the origin.[2,3]

Effect of Organic Substrate

On increasing the concentration of CA (0.05–0.2M), the rate of polymerization, $R_{p(obs)}$, increased.[10,16] The plots of $R_{p(obs)}$ versus [CA] (Fig. 4) are linear and have passed through the origin, supporting our kinetic scheme.[9a] The effect of other polyhydroxylic substrates on the rate were examined and compared with that of CA. The sequence was found to be in the order of sorbitol ≥ mannitol > glycerol > citric acid (Fig. 4). Some workers[1a] have reported the same trend of reactivity of these substrates on R_p. The redox action of the polyols is most likely facilitated by the number of hydroxyl groups, as there is a direct correlation between the number of hydroxyl groups and $R_{p(obs)}$ (Fig. 4) in this study. A higher number of hydroxyl groups promotes redox more effectively, thereby increasing radical flux and hence $R_{p(obs)}$. The $-R_{Ce(obs)}$ also increases on increasing the substrate concentration. The plot of $-R_{Ce(obs)}$ versus [sub-

strate] has also shown a straight line passing through the origin, which is according to eq. (2)[1a].

Effect of [H$^+$]

The increase in concentration of acid leads to a decrease in the rate, $R_{p(obs)}$, at a constant ionic strength (μ = 0.5M). But $R_{p(obs)}$ was independent of [H$^+$] when ionic strength was not maintained (Table II). This may be attributed to the formation of less active Ce(IV) species given by the following equilibrium, as suggested by Hardwick and Robertson[27]:

$$Ce(IV) + HSO_4^- \rightleftharpoons Ce(SO_4)(II) + H^+$$
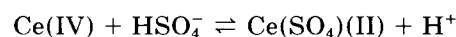
At constant [HSO$_4^-$], the increase in (H$^+$] will lead to a decrease in the ratio Ce(SO$_4$) (II)/Ce(IV). Hence with lower [H$^+$], the reactivity Ce(SO$_4$) (II) predominates whereas at higher [H$^+$], the effect is reversed.[1,28,29] The rate of Ce(IV) disappearance ($-R_{Ce}$) was also found to decrease on increasing [acid] at constant ionic strength. Other workers[28] have also observed similar types of changes while studying oxidation of citric acid by Ce(IV).

Effect of Temperature

The rate of enhancement of polymerization has also been seen on increasing the temperature from 30 to
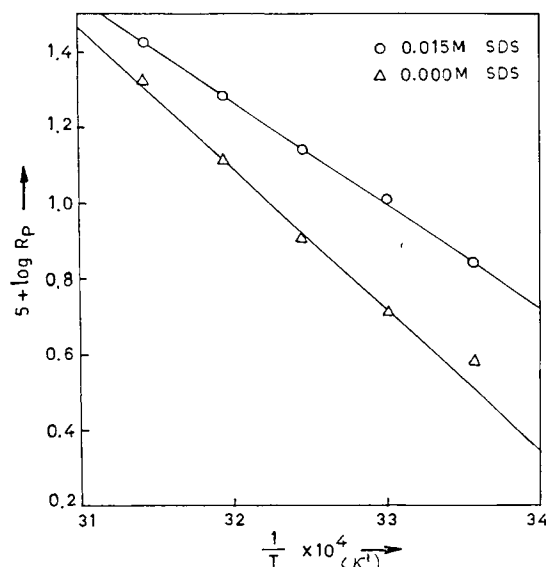

Figure 5 Arrhenius plot: log R_p vs. 1/T. [AN] = 0.694M; [Ce(IV)] = 5.01 × 10^{-3}M; [CA] = 0.108M; [H$^+$] = 0.495M; μ = 0.5M; temperature = 35°C.

45°C with and without SDS in reaction mixture. The solubilization of AN and CA increases on increasing the temperature, resulting in an acceleration of rate. From a plot of log $R_{p(obs)}$ versus $1/T$ (Fig. 5), the overall activation energy for the process was computed to be 18.31 and 13.72 kcal/mol in the absence and presence of $0.015M$ SDS, respectively. The overall decrease in activation energy of polymerization in the presence of surfactant indicates positive catalysis due to micelles.[9,10]

Chain Length

The molecular weight (M_w) of the polymers was determined viscometrically using Mark–Howink relationship[30]:

$$[\eta] = 2.43 \times 10^{-4}[M_w]^{0.75} \text{ (in DMF)}$$

where η is the intrinsic viscosities at 25°C.

The chain length of the polymer was calculated from M_w and found to increase on increasing SDS concentration (Table III). A similar result has been reported by Kim[31] while studying the effect of CTAB on polymerization of acrylamide and methyl acrylate initiated by sodium bisulfite.

CONCLUSION

The increase in the rate of polymerization and percentage of conversion of monomers to yield polymers in the presence of SDS is probably due to greater solubilization of monomers and citric acid molecules in the micellar phase for hydrophobic interaction. In addition, due to coulombic interaction of anionic micelles, the increased concentration of Ce(IV) may become more favorable to catalyze this polymerization.

REFERENCES

1. (a) A. Rout, S. P. Rout, B. C. Singh, and M. Santappa, *Makromol. Chem.*, **178**, 639 (1977); (b) S. P. Rout, A. Rout, N. Mallick, B. C. Singh, and M. Santappa, *Makromol. Chem.*, **178**, 1971 (1977); (c) S. V. Subramanian and M. Santappa, *J. Polym. Sci. Part A, 6*, 493 (1968).

2. K. N. Rao, B. Sethuram, and T. N. Rao, *Ind. J. Chem.*, **19A**, 259 (1980).

3. (a) G. S. Mishra and J. I. Khatib, *J. Ind. Chem. Soc.*, **59**, 1384 (1982); (b) G. S. Mishra, P. S. Bassi, and S. L. Abrol, *Ind. J. Chem.*, **22A**, 286 (1983).

4. (a) M. D. Fernadez and G. M. Guzman, *Eur. Polym. J.*, **25**, 1165 (1989); (b) M. D. Fernadez and G. M. Guzman, *Br. Polym. J.*, **22**, 1 (1990).

5. A. Goceman and B. Basaran, *Acta Polym.*, **42**, 675 (1991).

6. (a) C. Erbil, A. B. Soydan, and A. S. Sarac, *J. Appl. Polym. Sci.*, **47**, 1643 (1993); (b) C. Erbil, A. B. Soydan, Z. A. Arguz, and A. S. Sarac, *Angew Makromol. Chem.*, **213**, 55 (1993).

7. U. Tunaca, *J. Appl. Polym. Sci.*, **52**, 1491 (1994).

8. (a) C. M. Paleos and Ph. Dais, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 1495 (1978); (b) C. M. Paleos, Ph. Dais, and A. Malliaris, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3383 (1984); (c) C. M. Paleos, S. Voliotis, G. M. Leonidopoulous, and Ph. Dais, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 3463 (1980).

9. (a) N. Patel, I. Mohammed, B. N. Das, and B. K. Sinha, *J. Appl. Polym. Sci.*, **27**, 3859 (1982); (b) R. B. Panda, N. Patel, and B. K. Sinha, *J. Appl. Polym. Sci.*, **35**, 2193 (1988).

10. C. M. Patra and B. C. Singh, *J. Appl. Polym. Sci.*, **52**, 1549 (1994).

11. C. S. Larrabee and E. D. Sparque, *J. Polym. Sci. Polym. Lett. ED.*, **17**, 749 (1979).

12. S. Lenka and A. K. Dhal, *Eup. Polym. J.*, **18**, 342 (1982).

13. U. D. N. Bajpai, A. K. Bajpai, and J. Bajpai, *J. Ind. Chem. Soc.*, **69**, 841 (1992).

14. (a) M. Haruda, H. Namura, H. Kojima, N. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **16**, 811 (1972); (b) H. Namura, M. Haruda, H. Kojima, N. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **16**, 835 (1972).

15. (a) P. Bataille, B. T. Van, and Q. B. Pham, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 811 (1982); (b) F. Bataille, P. Bataille, and R. Fortin, *J. Polym. Sci. Chem. Ed.*, **26**, 1471 (1988).

16. S. P. Chatarjee, M. Banarjee, and R. S. Konar, *Ind. J. Chem.*, **19A**, 183 (1980).

17. S. Badran, A. B. Moustafa, A. A. Yehia, and S. M. H. Shendy, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 411 (1990).

18. A. Jayakrishnan and D. O. Shah, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 3201 (1983).

19. I. Capeg, *Polym. J.*, **26**, 1154 (1994).

20. M. B. Taylor, R. D. Gilbert, V. T. Stannet, and J. L. William, *J. Appl. Polym. Sci.*, **53**, 1385 (1994).

21. J. Barton, J. Tino, Z. Hlouskova, and M. Stillhammerova, *Polym. Int.*, **34**, 89 (1994).

22. A. Jayakrishnan and D. O. Shah, *J. Polym. Sci. Polym. Lett. Ed.,* **22,** 31 (1984).

23. F. W. Billmeyer, *Test Book of Polymer Science,* John Willey & Sons, Singapore, 1984, p. 209.

24. J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Microemulsion Systems,* Academic Press, New York, 1975, p. 21.

25. *CRC Handbook of Chemistry and Physics,* 73rd ed., CRC Press, Boca Raton, FL, 1992, pp. 16–22.

26. (a) K. Behari, G. D. Raja, and A. Agrawala, *Polymer,* **30,** 726 (1989); (b) K. Behari, U. Agrawala, R. Das, and L. Bahadur, *J. Makromol. Sci.,* **52,** 1549 (1994).

27. T. J. Hardwick and E. Robertson, *Can. J. Chem.,* **29,** 828 (1951).

28. S. N. Tripathy and R. K. Prasad, *Ind. J. Chem.,* **19A,** 214 (1980).

29. A. A. Katai, V. K. Kulashrestha, and R. H. Marchessault, *J. Polym. Sci. Sec. C,* **2,** 403 (1963).

30. W. H. Stockmayer and R. C. Cleland, *J. Polym. Sci.,* **17,** 437 (1955).

31. O. K. Kim, *Micellisation, Solubilisation and Microemulsion,* Vol. 2, K. L. Mittal, Ed., Phenum Press, New York, 1979, p. 627.