

Effect of Sodium Lauryl Sulfate on the Polymerization of Acrylonitrile

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Synopsis

Micellar catalyzed polymerization of acrylonitrile using ceric(IV)–glycerol redox system in aqueous sulfuric acid solution in the presence of sodium lauryl sulfate (NaLS) has been studied. The polymerization experiments were conducted between 15°C and 25°C, under conditions where no oxidation of sodium lauryl sulfate by ceric ion would be expected. The rate of polymerization (R_p) increases with increasing concentration of NaLS. The rate of monomer (AN) disappearance was proportional to $[\text{AN}]^{1.5}$ and $[\text{glycerol}]^{0.5}$, but, however, R_p changes in a nonlinear manner with increase in Ce(IV) concentration in the presence of the surfactant. The rate of Ce(IV) disappearance was not proportional to its original concentration. The chain length of the polymer could not be determined viscometrically, as the polymer obtained in presence of NaLS was insoluble in organic solvents. The activation energy of this polymerization process was calculated by conducting the experiment at different temperatures. The infrared spectra of the polymers in the presence and absence of surfactant have also been examined.

INTRODUCTION

A large number of articles have been published on the kinetic studies of vinyl polymerization using various redox systems and different monomers. Suitable organometallic compounds¹ and metal complexes² have also been used as initiators. Santappa et al. and others have vividly studied the vinyl polymerization using Ce(IV) as the initiator.³ These workers have studied the kinetics of polymerization by varying the composition of the reaction mixtures. However, little attention has been given to examine the effect of surfactants on such polymerization processes. Recently, Chatterjee et al.⁴ have studied the emulsion polymerization of styrene initiated by potassium persulfate. In the present work, attempts have been made to study the effect of NaLS on polymerization of acrylonitrile initiated by Ce(IV) and glycerol redox system.

EXPERIMENTAL

Reagents

Acrylonitrile (BDH) was purified by washing with 5% NaOH, 3% orthophosphoric acid and finally with water, followed by drying over fused CaCl_2 . Then, it was distilled in an atmosphere of nitrogen. Sodium lauryl sulfate (BDH) was purified according to the method of Duynstee and Grunwald.⁵ Ceric ammonium sulfate, glycerol, sodium hydroxide, and sulfuric acid were of analar grade and were used as such. Triply distilled water which was free from oxygen was used for preparation of solutions of the required concentration. The nitrogen used

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to deaerate the experimental system was freed from oxygen by passage through several columns of Fieser's solution, a column of saturated lead acetate solution and finally through a bottle containing oxygen-free triple distilled water.

ANALYSIS

Ceric ion concentration in stock solution was estimated by titration against a standard solution of Mohr's salt. The concentration of ceric ion in the experimental system was done by cerimetry using ferroin as indicator.

Experimental Setup and Procedure

The polymerizations were carried out in pyrex tubes of 100-mL capacity which were sealed at the bottom and fitted at the top with standard joints carrying inlet and outlet tubes for nitrogen. The stopper was also fitted with a microburette. The aqueous mixture of glycerol, sulfuric acid, acrylonitrile, sodium hydroxide (to maintain proper ionic strength by NaHSO_4), and sodium dodecyl sulfate were taken in the reaction tube. The total volume in the tube was constructed to be 20 mL. A wash bottle containing an aqueous solution of acrylonitrile of the same concentration as in the reaction tube was interposed between the nitrogen train and reaction vessel in order to compensate for the loss of monomer during deaeration. Nitrogen was bubbled through the reaction mixture for 30 min and stopcocks were closed. The reaction mixture was thermostated, and, when it attained the temperature of the bath, the required volume of ceric ammonium sulfate solution in 1M H_2SO_4 of appropriate concentration was added from the microburette. The polymerization started after a small interval of time and the reaction mixture becomes turbid. The reaction mixture was allowed to stand undisturbed and after definite intervals of time the reaction was quenched by addition of excess of standard ferrous ammonium sulfate solution. The polymer obtained was estimated gravimetrically. The filtrate was analyzed for residual cerium by cerimetry. The rate of polymerization (R_p) was calculated from the initial slope of the time conversion curve. The rate of disappearance of ceric ion ($-R_{Ce}$) was computed from the initial slope of the plot of Ce(IV) consumed vs. time.

RESULTS AND DISCUSSION

The most interesting observations made in the study are (i) increase of rate of polymerization with the increase of surfactant concentration, (ii) increase of percent conversion with the increase of $[\text{NaLS}]$, and (iii) change of nature of the polymer in the presence of surfactants. The relation between the percentage conversion and reaction time and rate of polymerization and $[\text{NaLS}]$ have been shown in Table I and Figures 1 and 2. Surfactants beyond their critical micelle concentration (cmc) form aggregates⁶ (micelles), and hence a biphasic system results. This system affects the nature of the chemical reaction. The yield of polyacrylonitrile increases with respect to the time, and it remains almost constant after 120 min in the presence of NaLS. This reaction has also been studied at different concentrations of monomer, ceric ion, and glycerol in presence of a fixed concentration of NaLS. The temperature effect at a $[\text{NaLS}]$ of 0.01M

TABLE I
Relation of Percentage Conversion with Time in Presence of Varying Concentration of NaLS in Polymerization of Acrylonitrile and Rate of Monomer Disappearance (R_p)^a

Time (min)	Percentage conversion				
	$10^3 \times [\text{NaLS}] (M)$				
	0	10	20	30	40
20	3.5	8.3	23.14	30.8	32.45
40	12.81	27.05	42.5	63.36	65.52
60	27.5	42.85	56.11	68.77	72.14
80	39.52	52.4	65.2	74.2	79.66
100	48.43	—	73.35	77.76	—
120	—	65.13	73.1	80.13	82.75
140	—	66.61	73.55	—	—
160	—	66.58	—	—	—
	$10^5 \times R_p (\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1})$				
	4.08	8.76	11.82	15.4	16.8

^a $[\text{Ce(IV)}] = 5.0 \times 10^{-3}M$, $[\text{AN}] = 0.72M$, $[\text{H}_2\text{SO}_4] = 0.36M$, $[\text{glycerol}] = 0.35M$. Temp = 20°C.

on the polymerization has been examined at 15–25°C. The conversion of monomer to form the polymer at 20–40 min was considerably increased in the presence of varying concentration of NaLS. However, the difference between % conversion in the absence and presence of NaLS decreases, when the polymerization is allowed to proceed for longer period, i.e., beyond 40 min. The polymer obtained in presence of NaLS is found to be insoluble in organic solvents; hence other polymeric properties could not be studied whereas the polymer obtained in the absence of NaLS is soluble in DMF. From IR spectra it became clear that the cyanide group is present ($\nu = 2240 \text{ cm}^{-1}$) in the polymers obtained in the absence and presence of NaLS, and it was further concluded from IR spectra that glycerol residue is absent in the polymeric chain.

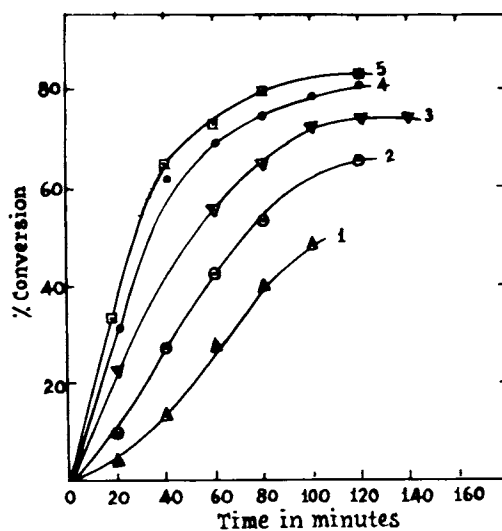
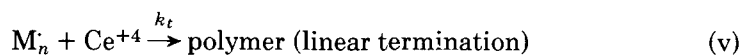
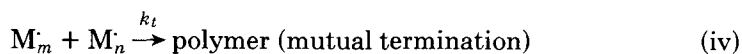
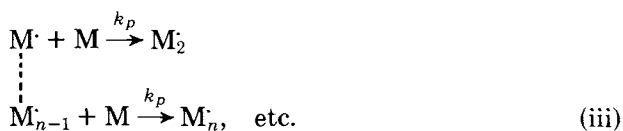
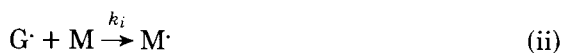
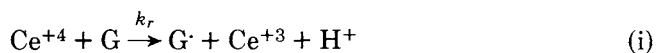


Fig. 1. Relation of % conversion in different NaLS concn: (1) 0.00M, (2) 0.01M; (3) 0.02M; (4) 0.03M; (5) 0.04M.

Effect of Surfactants

In the presence of the surfactant NaLS the polymerization process will occur in micellar phase and in the bulk phase. Hence the following schemes can be suggested.

Mechanism in Bulk Phase



(where G = glycerol and M = monomer, here acrylonitrile)

Making usual assumptions for the steady state concentrations of G· and M· and considering mutual termination the following rate expressions for R_p and $-R_{\text{Ce}}$ can be derived. In most of the experiments the concentration of Ce^{+4} is very low and hence initiation and termination by Ce^{+4} are expected to be very small. If one accepts that these possibilities have been eliminated, one may write:

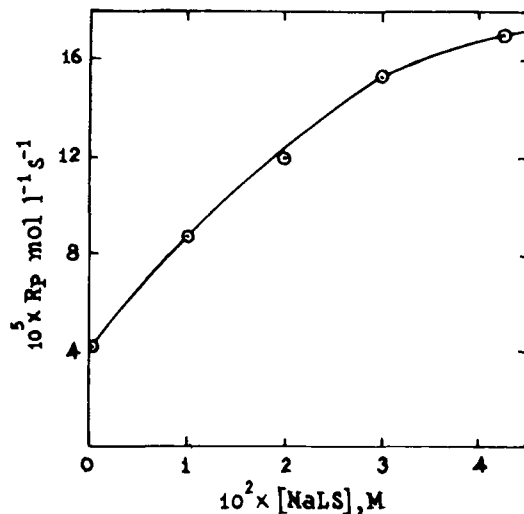


Fig. 2. Variation of R_p with [NaLS].

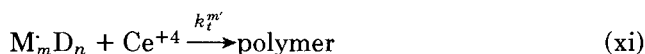
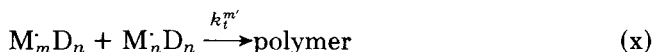
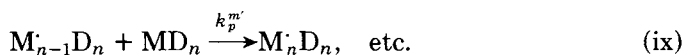
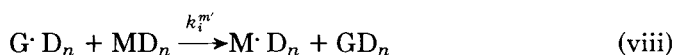
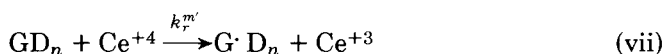
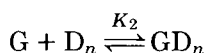
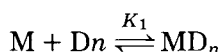
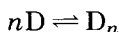
$$R_p = \frac{k_p [M]^{3/2} [Ce^{+4}]^{1/2}}{k_t^{1/2}} \left(\frac{k_r [G]}{[M] + (k_0/k_i) [Ce^{+4}]} \right)^{1/2} \quad (1)$$

and

$$-R_{Ce} = \frac{-d[Ce^{+4}]}{dt} = [Ce^{+4}] (k_r [G]) \quad (2)$$

Mechanism in Micellar Phase

In this phase the following equilibria can be assumed:



(where D = detergent, D_n = micelle, and superscript m' indicates the micellar phase).

By analogy with the expression derived for R_p in the bulk phase, a similar expression for $R_p^{m'}$ (rate of polymerization in micellar phase) can be written as follows:

$$R_p^{m'} = \frac{k_p^{m'} [MD_n]^{3/2} [Ce^{+4}]^{1/2}}{(k_t^{m'})^{1/2}} \left(\frac{k_r^{m'} [GD_n]}{[MD_n] + (k_0^{m'}/k_i^{m'}) [Ce^{+4}]} \right)^{1/2} \quad (3)$$

The overall polymerization rate $R_{p(\text{obv})}$ can be assumed as the sum of the rates of polymerization in bulk phase (R_p) and that in the micellar phase ($R_p^{m'}$), i.e., $R_{p(\text{obv})} = R_p + R_p^{m'}$. But, at higher concentration of surfactant far beyond its cmc, $R_{p(\text{obv})}$ can be assumed to be equal to $R_p^{m'}$.

On substituting the values of MD_n and GD_n , squaring both sides and taking

TABLE II
Rate of Monomer Disappearance (R_p) and of Ce(IV) Disappearance in Polymerization of Acrylonitrile in Presence of NaLS^a

$10^2 \times [\text{AN}]$ (M)	$10^5 \times R_p$ ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)	$10^5 \times -R_{\text{Ce}}$ ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)
30	4.75	3.3
45	9.00	2.4
60	15.5	2.08
75	20.62	1.52

^a $[\text{Ce(IV)}] = 4.8 \times 10^{-3}M$, $[\text{H}_2\text{SO}_4] = 0.35M$, $[\text{glycerol}] = 0.7M$, $[\text{NaLS}] = 0.04M$. Temp = 20°C.

reciprocals the eq. (3) can be rearranged to

$$\frac{[\text{M}]^2}{[R_{p(\text{obv})}]^2} = \frac{k_t^{m'}}{(k_p^{m'})^2 k_r^{m'} K_1^2 K_2 [\text{D}_n]^3 [\text{G}][\text{Ce}^{+4}]} + \frac{k_t^{m'} k_0^{m'}}{(k_p^{m'})^2 k_r^{m'} k_i^{m'} K_1^3 K_2 [\text{D}_n]^4 [\text{M}][\text{G}]} \quad (4)$$

From the plot of $[\text{M}]^2/[R_{p(\text{obv})}]^2$ vs. $1/[\text{M}]$, the slope to intercept ratio will be given by $k_0^{m'}[\text{Ce}^{+4}]/k_i^{m'}K_1[\text{D}_n]$, and the intercept will be the first term of the expression of the right-hand side of eq. (4). Assuming the relative catalysis of surfactant to be same, and, using the values of composite constants k_0/k_i , k_r , and $k_t/(k_p)^{1/2}$ of Santappa et al.,^{3b} the values of association constants K_1 and K_2 have been calculated to be $7.6 \times 10^2 \text{ mol}^{-1}\cdot\text{L}$ and $2.28 \times 10^4 \text{ mol}^{-1}\cdot\text{L}$, respectively. In order to calculate $[\text{D}_n]$, using the expression $[\text{D}_n] = C_D - \text{cmc}/N$; the aggregation number N has been taken to be 62.⁶

Rate of Monomer Disappearance

The value of $R_{p(\text{obv})}$ was found to be proportional to $[\text{M}]^{3/2}$ and $[\text{G}]^{1/2}$ (Tables II and III). The rates of polymerization also increases initially with increase of $[\text{Ce(IV)}]$ but decreases above a certain concentration of ceric salt (Table IV). Similar observations have been reported⁷ in case of aqueous polymerization of acrylamide. The plot of $R_{p(\text{obv})}$ vs. $[\text{M}]^{3/2}$ is a straight line passing through the origin supports the view that termination by Ce(IV) at its low concentration can be ruled out. With certain approximations, eq. (1) can be rearranged and the validity was verified. A plot of R_p^2 vs. $[\text{G}]$ resulted in a straight line with an intercept indicating that polymerization is possible in the absence of glycerol and termination is mutual.

TABLE III
Effect of $[\text{Glycerol}]$ on Rate of Polymerization in Presence of NaLS at 20°C^a

$[\text{glycerol}]$ (M)	$10^5 \times R_p$ ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)	$10^5 \times -R_{\text{Ce}}$ ($\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$)
0.7	17.05	1.50
1.05	19.79	1.96
1.40	22.73	2.5

^a $10^3 \times [\text{Ce(IV)}] = 4.8M$, $[\text{H}_2\text{SO}_4] = 0.35M$, $[\text{AN}] = 0.75M$, $[\text{NaLS}] = 0.04M$.

TABLE IV
Effect of [Ce(IV)] on Rate of Polymerization in Presence of NaLS at 20°C^a

$10^3 \times [\text{Ce(IV)}]$ (M)	$10^5 \times R_p$ (mol·L ⁻¹ ·s ⁻¹)	$10^6 \times -R_{\text{Ce}}$ (mol·L ⁻¹ ·s ⁻¹)
2.5	12.5	9.18
5.0	20.62	18.33
10	22.73	19.58
15	15.00	11.11

^a [AN] = 0.06M, [H₂SO₄] = 0.35M, [glycerol] = 0.7M, [NaLS] = 0.04M.

Rate of Ceric Disappearance

A plot of R_p vs. [Ce(IV)] is not a linear one, and the rate of Ce⁺⁴ disappearance was not directly proportional to the concentration of Ce(IV) (Table IV). Santappa et al.^{3b} have observed that $-R_{\text{Ce}}$ (rate of Ce⁺⁴ disappearance) is directly proportional to [Ce(IV)]. As the present study was done in the presence of an anionic surfactant micelle, some Ce⁺⁴ must be entering into the Stern layer, and hence its disappearance was not proportional.

Effect of Temperature

The rate of polymerization and percent conversion increased by increasing the temperature in presence of 0.01M NaLS in the reaction mixture. The rate of Ce⁺⁴ disappearance also increased on raising the temperature from 15°C to 25°C (Table V). The enhancement is due to the increased solubilization of the monomer in the micellar phase. A plot of the logarithmic rate of polymerization against the reciprocal of the absolute temperature in the range 15–25°C gave 12.3 kcal/mol as the overall activation energy for acrylonitrile polymerization in the presence of sodium lauryl sulfate.

TABLE V
Variation of R_p and $-R_{\text{Ce}}$ with Change in Temperature in Presence of 0.01M NaLS^a

Temp (°C)	$10^5 \times R_p$ (mol·L ⁻¹ ·s ⁻¹)	$10^6 \times -R_{\text{Ce}}$ (mol·L ⁻¹ ·s ⁻¹)
15	6.7	—
20	9.2	8.33
25	13.00	12.5

^a $10^3 \times [\text{Ce(IV)}] = 5.0M$, [AN] = 0.6M, [glycerol] = 0.7M, [H₂SO₄] = 0.35M.

CONCLUSION

The increase in the rate of polymerization and yield of polymer in presence of NaLS is probably due to, first, the greater solubilization of monomer molecules and glycerol in the micellar phase due to hydrophobic interactions. Konar et al.⁴ have studied the emulsion polymerization of styrene initiated with potassium persulfate and have offered a similar explanation. Secondly, due to coulombic interaction, the initiation by Ce⁺⁴ will be more favourable as concentration of Ce⁺⁴ increases in the Stern layer of the anionic micelles.

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