

Polymerization of Methyl Methacrylate in Micellar Phase: A Kinetic Study

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Synopsis

Polymerization of methyl methacrylate (MMA) using Ce(IV) as initiator in aqueous nitric acid solution in the presence of sodium lauryl sulphate (NaLS) has been studied kinetically at a temperature range of 25–35°C. The rate of polymerization (R_p) increases with increasing concentration of NaLS, and it was also proportional to $[MMA]^2$; but, in the presence of NaLS, the change of R_p with respect to $[Ce(IV)]$ and $[H^+]$ were not linear and similarly the rate of Ce(IV) disappearance was not proportional to its original concentration. The overall activation energy of the polymerization process in presence of 0.01M NaLS was found to decrease by ~ 7.0 kcal mol⁻¹. The monomer-micelle association constant has been calculated to be 5.135×10^4 mol⁻¹ L. The polymer obtained in surfactant medium is sparingly soluble in benzene and DMSO. From infrared spectra clear evidence of vinyl polymerization was obtained.

INTRODUCTION

During the last five years some amount of work has been done on polymerization kinetics in the presence of surfactants. Jayakrishnan and Shah^{1,2} have studied the emulsion and microemulsion polymerization of some vinyl monomers in the presence of surfactants. Polymerization of vinyl monomers in aqueous surfactant solutions have been studied by some workers. We³ have reported the solution polymerization of acrylonitrile in the presence of NaLS. The present work deals with the kinetic investigation of polymerization of MMA in the presence of NaLS in order to gather additional information regarding the mechanism.

EXPERIMENTAL

Reagents

Methyl methacrylate was purified by washing with 25% alkali solution and distilled repeatedly in an atmosphere of nitrogen *in vacuo*.⁴ Sodium lauryl sulfate (BDH) was purified by the method suggested by Duynstee and Grunwald.⁵ Analar grade ceric ammonium nitrate, sodium hydroxide, and nitric acid were used without further purification. Oxygen-free triply distilled water was used for preparation of solutions. The nitrogen 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 triple distilled water.

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Analysis

Ceric ion concentration in stock solution was estimated by titration against standard solution of Mohr's salt. The concentration of ceric ion in the experimental system was determined by cerimetry using *N*-phenyl anthranilic acid as indicator.

Experimental Setup and Procedure

The experimental setup and kinetic measurements are similar to our earlier report.³ The only difference is that the reaction has been arrested at a definite interval of time by chilling, and the polymer has then been filtered immediately into a known volume of excess standard Mohr's salt solution in order to estimate the consumption of Ce(IV). The rate of polymerization (R_p) and rate of ceric ion disappearance ($-R_{Ce}$) have been calculated from the initial slopes of the time conversion curve of monomer and plot of Ce(IV) consumption vs. time, respectively. The ionic strength has been maintained in the reaction mixture by indirect addition of NaNO_3 .

RESULTS AND DISCUSSION

The polymerization of methyl methacrylate (MMA) has been studied in the presence of sodium lauryl sulfate using Ce(IV) as the initiator. No additional organic substrate has been taken for free radical formation. The important observations are (i) increase of rate of polymerization by increasing the concentration of NaLS and (ii) increase of percent conversion of monomer with increase of [NaLS]. The kinetic results of polymerization in the absence and presence of NaLS have been compared relating to some parameters. The percentage conversion has also been studied at varying concentrations of monomer, ceric ion, nitric acid, and temperature in the presence of 0.01M NaLS. Although at higher surfactant concentration both the rate of polymerization and the yield of polymer are greater due to slow rate of filtration, most of the experiments were carried on at 0.01M NaLS. Beyond 0.03M [NaLS] the experiments could not be carried on successfully.

Effect of Surfactant

The variation of the percentage conversion with respect to time in the polymerization of MMA initiated by Ce(IV) in the absence and presence of varying concentration of NaLS at 35°C has been shown in Table I. The rate of polymerization (R_p) has been calculated from the initial slope of the time conversion curve, and the values are also given in Table I. It is observed that the rate of polymerization and yield of polymer increases by addition of NaLS when its concentration increases from 0.01 to 0.03M (Fig. 1). The increase in percentage conversion is not very significant after a time period of 60 min in most of the cases. It is known definitely that in an aqueous medium, surfactants beyond their critical micelle concentration (cmc) form aggregates, and a biphasic system is created, namely, bulk phase and micellar pseudo phase. This affects the rate of polymerization. Due to hydrophobic interaction of NaLS micelles, the monomers get concentrated in the micelle and [Ce(IV)] also increases in the stern layer due to electrostatic attraction. As a result of this,

TABLE I
Relation of Percentage Conversion with Time in Presence of Varying Concentration of NaLS in Polymerization of MMA and Corresponding R_p and $-R_{Ce}$ Values^a

| Time (min) | Percentage conversion | | | |
|------------|-----------------------|---|-------|-------|
| | 0 | 10 | 20 | 30 |
| | | $10^3 \times \text{NaLS } (M)$ | | |
| 10 | — | 8.54 | 14.35 | 17.95 |
| 15 | — | — | 17.23 | 18.91 |
| 20 | 6.71 | 16.43 | 20.12 | 22.34 |
| 30 | 8.83 | 17.19 | — | — |
| 40 | 13.59 | 19.82 | 22.5 | 27.5 |
| 60 | 15.71 | 21.94 | — | — |
| | | $10^6 \times R_p (\text{mol L}^{-1} \text{s}^{-1})$ | | |
| | 6.70 | 15.87 | 26.75 | 28.13 |
| | | $10^7 \times -R_{Ce} (\text{mol L}^{-1} \text{s}^{-1})$ | | |
| | 0.51 | 2.33 | 2.50 | 3.12 |

^a $[\text{Ce(IV)}] = 6.75 \times 10^{-3}M$, $[\text{MMA}] = 0.1125M$, $[\text{HNO}_3] = 0.23M$, $\text{temp} = 35^\circ\text{C}$.

the rate of polymerization as well as the yield of polymer increases, regardless of the shape and the size of the micelle. Owing to the complexities of micellar structure, which depends on a large number of parameters, it is difficult to predict which type of micelles are involved in our process.

Ananthanarayan and Santappa⁶ have proposed a kinetic scheme for polymerization of MMA which can be applied for the polymerization taking place in bulk phase. The process is initiated by a free radical, resulting from the action of Ce(IV) on monomer. Making the usual assumption for the steady state concentration of monomer radical, the rate of monomer disappearance

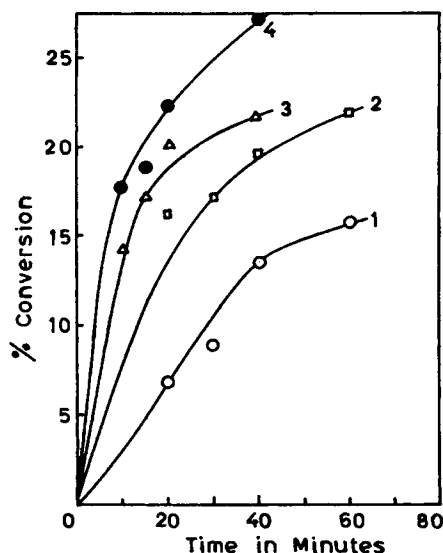


Fig. 1. Relation of % conversion in different NaLS concn: (1) 0.00M; (2) 0.01M; (3) 0.02M; (4) 0.03M.

(R_p) and rate of Ce(IV) disappearance can respectively be represented by

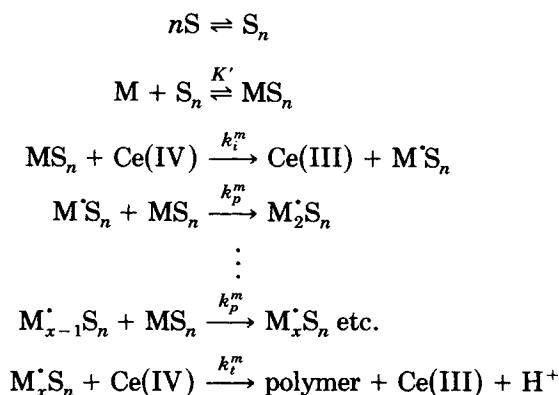
$$R_p = -\frac{d[M]}{dt} = \frac{k_i k_p}{k_t} [M]^2 \quad (1)$$

$$-R_{\text{Ce}} = -\frac{d[\text{Ce(IV)}]}{dt} = 2k_i [M][\text{Ce(IV)}][\text{H}^+]/(K + [\text{H}^+]) \quad (2)$$

(where M = monomer, k_i , k_p , and k_t are rate constants for initiation, propagation, and termination steps of polymerization and K is hydrolytic equilibrium constant in Ce(IV) and H_2O equilibrium).

Rout et al.⁷ have confirmed in numerous publications that vinyl polymerizations initiated by redox systems proceed by chain reaction mechanism. The polymer is formed either by mutual or linear termination step, depending on the experimental conditions. Hence kinetic schemes proposed by them are acceptable. In our earlier work³ we have adopted such a kinetic scheme involving micelle (D_n), monomer-micelle complex (MD_n), and formation of its radical, etc., applicable to micellar pseudo phase and have derived a certain expression that fits the experimental data well. Another group of workers⁸ have reported a positive micellar effect of NaLS on the polymerization of styrene. Jayakrishnan and Shah^{1,2} have also carried on the polymerization of vinyl monomers in the presence of surfactant in different media where they have predicted the possibility of involvement of micelles in the polymerization process.

Therefore, in the micellar phase the following sequence of reaction can be assumed:



(where S = surfactant, S_n = micelle, K' = association constant, and the superscript m indicates the micellar phase).

Now the rate of polymerization and that of Ce(IV) disappearance in the micellar phase can be represented by the following equations:

$$R_p^m = \frac{k_i^m k_p^m}{k_t^m} [MS_n]^2 \quad (3)$$

$$-R_{\text{Ce(IV)}}^m = 2k_i^m [MS_n][\text{Ce(IV)}][\text{H}^+]/(K' + [\text{H}^+]) \quad (4)$$

TABLE II
Rate of Monomer Disappearance (R_p) and of Ce(IV) Disappearance in Polymerization of Methyl Methacrylate at Varying Concentration in Presence of NaLS^a

| $10^2 \times [\text{MMA}]$ (M) | $10^6 \times R_p$ ($\text{mol L}^{-1} \text{s}^{-1}$) | $10^7 \times -R_{\text{Ce}}$ ($\text{mol L}^{-1} \text{s}^{-1}$) |
|---------------------------------------|--|---|
| 7.5 | 6.25 | 1.90 |
| 9.0 | 10.00 | 2.11 |
| 11.25 | 15.87 | 2.33 |

^a $[\text{Ce(IV)}] = 6.75 \times 10^{-3}M$, $[\text{HNO}_3] = 0.23M$, $[\text{NaLS}] = 0.01M$, $\text{temp} = 35^\circ\text{C}$.

The $R_{p(\text{obs})}$ (the observed rate of polymerization in the presence of surfactant) can be assumed as the sum of the rates of polymerization in the bulk phase and in the micellar phase. But at higher concentrations of surfactant beyond its cmc it seems from our result that a negligible amount of polymerization takes place in the bulk phase. Hence, in the presence of surfactant above its cmc, $R_{p(\text{obs})}$ is almost equal to R_p^m . A plot of $R_{p(\text{obs})}$ vs. $[\text{M}]^2$ is a straight line that passes through the origin. This result supports the above assumptions. From the slope of this plot the value of $k_i^m k_p^m / k_t^m$ was calculated to be $11.54 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$. Substituting the value of MS_n in eq. (3) the value of K' was found to be $5.135 \times 10^4 \text{ mol}^{-1} \text{ L}$, where $[\text{S}_n] = (C_s - \text{cmc})/N$ and the value⁹ of N was taken to be 62. C_s stands for the concentration of NaLS.

The rate of polymerization (monomer disappearance) has been studied with increasing concentration of NaLS (Table I), increasing concentration of monomer (Table II), Ce(IV) (Table III), HNO_3 (Table IV) and raising temperature from 25 to 35°C (Table VI) at a fixed concentration of NaLS. A plot of R_p vs. $[\text{NaLS}]$ indicates that rate of polymerization increases with increasing con-

TABLE III
Effect of Ce(IV) on the Rate of Polymerization in Presence of NaLS^a

| $10^3 \times \text{Ce(IV)}$ (M) | $10^6 \times R_p$ ($\text{mol L}^{-1} \text{s}^{-1}$) | $10^7 \times -R_{\text{Ce}}$ ($\text{mol L}^{-1} \text{s}^{-1}$) |
|--|--|---|
| 6.75 | 15.87 | 2.33 |
| 8.00 | 21.15 | 2.50 |
| 10.00 | 26.04 | 2.83 |

^a $[\text{MMA}] = 0.1125M$, $[\text{HNO}_3] = 0.23M$, $[\text{NaLS}] = 0.01M$, $\text{temp} = 35^\circ\text{C}$.

TABLE IV
Effect of $[\text{HNO}_3]$ on the Rate of Polymerization in Presence of NaLS^a

| $10 \times [\text{HNO}_3]$ (M) | $10^6 \times R_p$ ($\text{mol L}^{-1} \text{s}^{-1}$) | $10^7 \times -R_{\text{Ce}}$ ($\text{mol L}^{-1} \text{s}^{-1}$) |
|---------------------------------------|--|---|
| 2.3 | 15.87 | 2.33 |
| 3.0 | 21.56 | 2.50 |
| 4.0 | 37.50 | 2.97 |

^a $[\text{MMA}] = 0.1125M$, $[\text{Ce(IV)}] = 6.75 \times 10^{-3}M$, $[\text{NaLS}] = 0.01M$, $\text{temp} = 35^\circ\text{C}$.

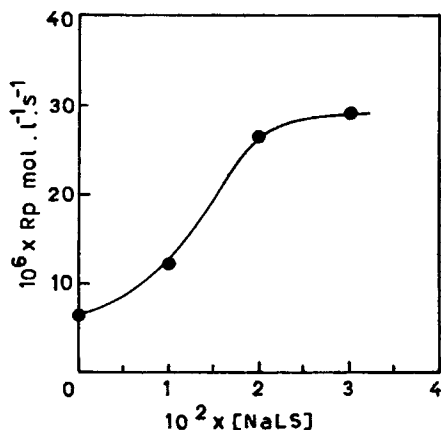


Fig. 2. Variation of R_p with $[\text{NaLS}]$.

centration of NaLS (Fig. 2). The rate of monomer disappearance bears a square dependence on the monomer concentration (Fig. 3), and it rules out the possibility of mutual termination. Hence eq. (3) is valid for this polymerization.

Rate of Ceric Ion Disappearance and Effect of $[\text{H}^+]$ in the Presence of NaLS on Polymerization

On increasing the concentration of Ce(IV), the rate of polymerization increases (Table III), but no linear plot was obtained out of R_p vs. $[\text{Ce(IV)}]$. The rate of Ce(IV) disappearance was not directly proportional to $[\text{Ce(IV)}]$ in the reaction mixture. It can also be seen from Table IV that R_p increases with increasing concentration of HNO_3 . From the plot of R_p vs. $[\text{H}^+]$ it became evident that there is no linear dependence of rate of polymerization on $[\text{H}^+]$. From these observations it is concluded that Eq. (4) does not fit the experimental results. The reason is that Ce(IV) ion and H^+ are not equally distributed in the bulk phase and micellar phase as the presence of anionic micelles regulates their distribution.

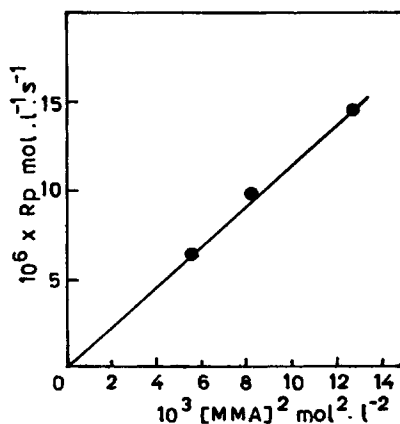


Fig. 3. Variation of R_p with $[\text{monomer}]^2$.

TABLE V
Variation of R_p and $-R_{Ce}$ with Change in Temperature in Absence of NaLS^a

| Temp (°C) | $10^6 \times R_p$ (mol L ⁻¹ s ⁻¹) | $10^7 \times -R_{Ce}$ (mol L ⁻¹ s ⁻¹) |
|--------------|---|---|
| 25 | 3.52 | 0.22 |
| 30 | 5.63 | 0.37 |
| 35 | 6.70 | 0.51 |

^a[MMA] = 0.1125M, [Ce(IV)] = 6.75×10^{-3} M, [HNO₃] = 0.23M.

TABLE VI
Variation of R_p and $-R_{Ce}$ with Change in Temperature in Presence of NaLS^a

| Temp (°C) | $10^6 \times R_p$ (mol L ⁻¹ s ⁻¹) | $10^7 \times -R_{Ce}$ (mol L ⁻¹ s ⁻¹) |
|--------------|---|---|
| 25 | 9.87 | 1.20 |
| 30 | 14.06 | 1.54 |
| 35 | 15.87 | 2.33 |

^a[MMA] = 0.1125M, [Ce(IV)] = 6.75×10^{-3} M, [HNO₃] = 0.23M, [NaLS] = 0.01M.

Effect of Temperature

The rate of polymerization and percent conversion increased by increasing the temperature from 25 to 35°C in the absence and presence of 0.01M NaLS. The observations have been recorded in Tables V and VI, respectively. The rate of Ce(IV) disappearance also increased on raising the temperature. The overall activation energy for MMA polymerization in the absence and presence of 0.01M NaLS was found from the plot of the log R_p vs. $1/T$ to be 10.83 and 3.84 kcal/mol, respectively. In the presence of 0.01M NaLS the activation energy has decreased by ~ 7.0 kcal/mol.

Other Observations

The solubility of the polymers obtained in the presence of NaLS was examined in a good number of organic solvents and was found sparingly soluble in benzene and DMSO. Due to the solubility problem, many properties of the polymer obtained by us could not be studied. The IR spectra of the polymer in the presence and absence of NaLS have been examined and compared with spectra of MMA. The absence of characteristic absorption at $\nu = 675\text{--}1000$ cm⁻¹ due to the out-of-plane bend of =C—H confirms the vinyl polymerization.

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