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# Polymerization kinetics of acrylamide in micelles and microemulsions

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The polymerization kinetics of acrylamide was investigated in the system of cetyltrimethyltetrammonium bromide–water micelles. The maximal polymerization rate was found at the second critical micelle concentration. A square-root dependence of the polymerization rates, $R_p$, on the initiator concentrations was obtained. Polymerization in microemulsions was also investigated to establish a connection between the structures of microemulsions and polymerization reaction rate. The microemulsions consisted of cetyltrimethylammonium bromide, n-butanol, n-octane and water. Their structures were determined by conductivity measurements. Our results showed that maximal polymerization rates occurred at two transition points from water in oil (W/O) to bicontinuous (BC) and from bicontinuous (BC) to oil in water (O/W). At the same time, we also found that the polyacrylamide molecular weights depended on the structures of microemulsions. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: acrylamide; polymerization kinetics; micelles)**

## INTRODUCTION

Catalysis or inhibition of solution reactions by surfactant micelles has been investigated for more than three decades following the pioneering work by Duynstee and Grunwald in 1959[1]. There has been steadily increasing number of investigations on the catalytic or inhibition effect of micelles by many authors, such as Friberg and Ahmad[2,3], and Broxton and Christie[4]. Micelles have been used as mimic enzymic catalysts and biocatalysts, which has attracted a lot of attention during recent years[5,6].

Microemulsions are transparent, isotropic and thermodynamically stable mixtures of oil and water stabilized by surfactant and usually with a cosurfactant[7]. In recent years, reactions in microemulsions have been considered of great interest[8,9], and the theoretical connection between the structure and its effects on the chemical reactions is an area of growing research[10,11]. It has been demonstrated that rather small changes in structure may give rise to a pronounced influence on the reaction rate[3]. So it is of great importance to the investigation of chemical reactions in systems which have different structures.

Polyacrylamide is a versatile material[12]. It can be used as a flocculating agent in dealing with drilling mud and waste water, and its most common use is as a thickening agent in enhancing oil recovery. But the properties of polyacrylamide and its potential uses are a function of its molecular weight and its molecular weight distribution (MWD). Therefore it is necessary to predict and control the polymerization process. Microemulsions provide a unique medium for polymerization of both hydrophilic and hydrophobic polymers in which molecular weight can be controlled and predicted. Although many studies on the kinetics of polymerization of acrylamide and its molecular weight have been reported in the literature[12,13], and many techniques for initiation of polymerization of acrylamide, such as $\gamma$-ray initiation, ultrasonic waves[14], photopolymerization[15], thermopolymerization[16] and azo[17] (free radia initiated by 4,4′-azo-bis-4-cyanopentamic acid), have been developed, few investigations have been reported for microemulsion systems.

Under these circumstances it was deemed worthwhile to undertake an explorative investigation on the reaction rates and molecular weight of polyacrylamide in micelles and the different microemulsion systems (water-in-oil (W/O), bicontinuous (BC), which involves fluid transparent isotropic media in equilibrium simultaneously with an excess water phase and an excess hydrocarbon phase, and oil-in-water (O/W)).

## EXPERIMENTAL

### *Materials*

Cetyltrimethyltetrammonium bromide (CTAB) was AR grade. It was recrystallized three times from ethanol (AR) and acetone (AR) mixed solvents, the volume ratio being 1 : 5. The product was dried under aspirator vacuum at 60°C for 6 h.

Acrylamide was also AR grade. It was recrystallized

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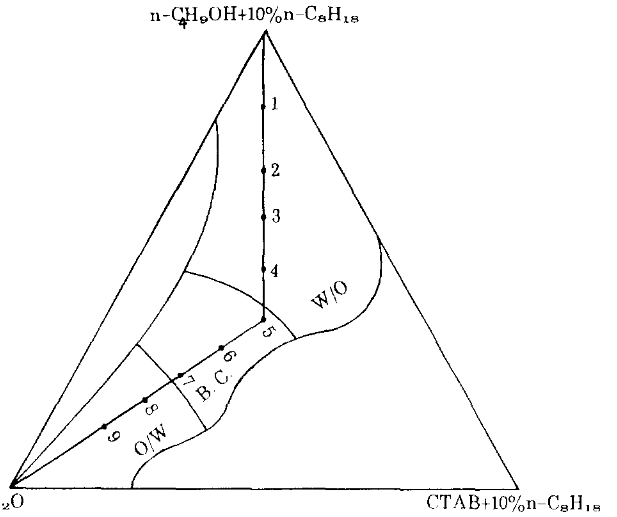


**Figure 1** The phase diagram and microemulsion structures in the system cetyltrimethyltetraammonium bromide/n-butanol/10% n-octane/water at 40°C. The composition of samples for which reaction rates were determined is indicated in the figure

three times from acetone, washed with benzene, and dried under aspirator vacuum at room temperature.

Initiator (sodium bisulfite, $NaHSO_3$) was a specially pure grade, and was used without further purification. All other chemicals were of analytical grade and were used as received. Water was doubly deionized and distilled.

### *Microemulsion regions*

Determination of phase boundaries was made by titrating with water various surfactant, n-butanol and n-octane mixtures at 40°C, first to the point of dissolution of surfactant, which marked the right-hand limit of the solubility region (see *Figure 1*), then to the first appearance of turbidity, which defined the left-hand limit. Using conductivity measurements[18], well-defined regions in the phase diagram of the microemulsion were identified corresponding to W/O, BC and O/W structures.

### *Polymerization rates*

The polymerization in micelles was carried out at 40°C in a four-necked glass flask containing a magnetic stirrer, and using sodium bisulfite ($NaHSO_3$) as initiator under a nitrogen atmosphere. After a certain reaction time (20 min), the polymerization was stopped with acetone. The polymerization rates were found by determining the amount of polymer which was washed with acetone and ethanol mixed solvent, and dried to a constant weight.

The polymerization in microemulsion was carried out at 30°C and 45°C, respectively. The microemulsion media were prepared by weighing the components according to the composition corresponding to a point on the line indicated in *Figure 1*, which passes through the W/O, BC and O/W phases.

### *Molecular weight determination*

Polyacrylamide molecular weights were determined at 30°C by viscosity measurements and application of the relationship[19] of molecular weight to intrinsic viscosity:

$$[\eta] = 6.31 \times 10^{-5} \bar{M}^{0.80} \qquad (1)$$

## RESULTS AND DISCUSSION

### *Polymerization of acrylamide in micelles*

*Dependence of polymerization rate on initiator.* The initial concentration of acrylamide is 1.4069 M, the concentration of CTAB is $2.000 \times 10^{-3}$ M, and the concentration of the initiator varies from $6.0 \times 10^{-5}$ to $1.0 \times 10^{-3}$ M. The polymeric time is 20 min. A plot of $\log R_p$ ($\mathrm{mol\,l^{-1}\,s^{-1}}$) vs. $\log C_{HSO_3}$ gives a straight line (see *Figure 2*). The slope of this straight line, 0.50, determines the catalyst exponent. It shows that the polymerization rate is dependent on the square root of the initiator concentrations. This dependence has been confirmed for many different monomer–initiator combinations over ranges of monomer and initiator concentrations[20].

*Effect of CTAB concentrations on polymerization rate.* The initial concentration of acrylamide is 1.4609 M, the concentration of initiator ($NaHSO_3$) is $2.000 \times 10^{-4}$ M, and the concentration of CTAB varies from $1.3170 \times 10^{-4}$ to $7.9998 \times 10^{-2}$ M. The dependence of $R_p$ on CTAB concentrations is illustrated in *Figure 3*. At concentrations of CTAB below the critical micelle concentration, CMC ($9.0 \times 10^{-4}$ M in water[5]), the $R_p$ is nearly the same as that of the aqueous solution. The $R_p$ increase is small in the CMC region but there is a pronounced rise in $R_p$ at [CTAB] = $8.0 \times 10^{-3}$ M, the second CMC, which is the transition concentration from spherical to

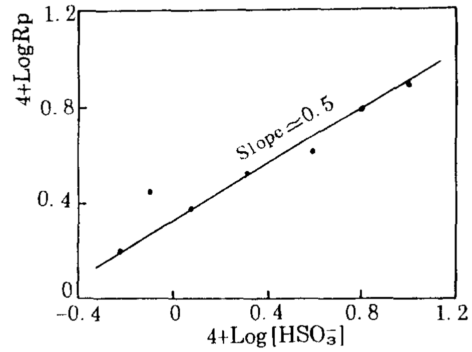


**Figure 2** Double logarithmic plot of the initial rate of polymerization, $R_p$ (in $\mathrm{mol\,l^{-1}\,s^{-1}}$) vs. concentrations of $NaHSO_3$ ($\mathrm{mol\,l^{-1}}$); [CTAB] = $2.00 \times 10^{-3}$ M, [acrylamide] = 1.4069 M, temperature = 40°C

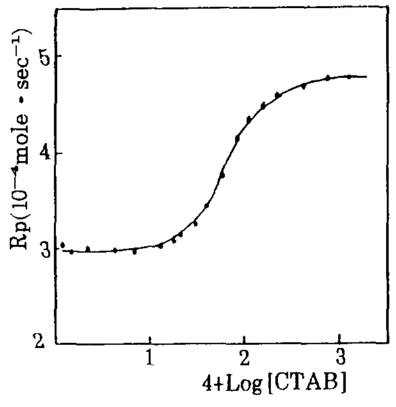


**Figure 3** Plot of the initial rate of polymerization, $R_p$ (in $\mathrm{mol\,l^{-1}\,s^{-1}}$) vs. the logarithm of CTAB concentrations; [$NaHSO_3$] = $2.00 \times 10^{-4}$ M, [acrylamide] = 1.4069 M, temperature = 40°C

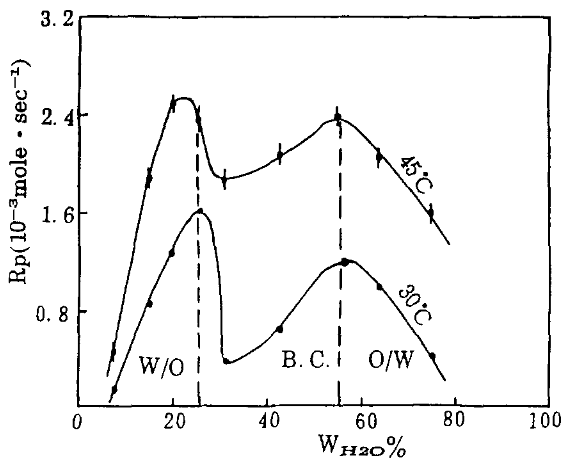


**Figure 4** The initial rate of polymerization $R_p$ (in $mol\,l^{-1}\,s^{-1}$) in microemulsion vs. water content as given in *Figure 1*; $[NaHSO_3] = 3.9101 \times 10^{-3}$ M, ratio of microemulsion volume to acrylamide weight = 10 ml : 2 g

rod-like micelles; it then approaches a limiting value with further increase of CTAB concentration.

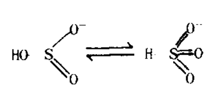
In most cases, detergent micelles are not directly involved in the reaction but affect the reactivity of a reagent through electrostatic and hydrophobic interactions, which are therefore dominant factors in the kinetics of micellar systems.

Acrylamide ($CH_2=CH-C(O)-NH_2$) is a strongly hydrophilic and non-ionic monomer, so that interaction between acrylamide and CTAB micelles is expected to be negligibly small. Accordingly, CTAB micellar interactions with acrylamide, if any, can be ascribed largely to bisulfite in the present polymerization system.

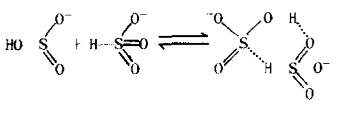
The mechanism of initiation by sodium bisulfite in the polymerization of acrylamide may be of the free-radical type[21]. The overall reaction can be written as

$$2HSO_3^- + \rangle C{=}C\langle + 2H_2O \rightarrow 2H\dot{S}O_3 + \rangle CH{-}CH\langle + 2OH^- \qquad (2)$$

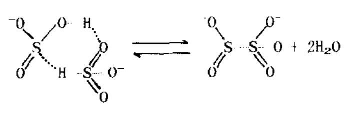
Golding[22] has shown by ultraviolet absorption spectroscopy that the equilibria in bisulfite must be considered:



low concentration (3)



high concentration (4)



(5)

In the CTAB micellar system, the changes in ionic equilibria of sodium bisulfite can be written as follows:

$$RR'_3N^+ + HSO_3^- \rightleftharpoons [RR'_3N^+ \cdots {}^-O_3SH] \qquad (6)$$

$$[RR'_3N^+ \cdots {}^-O_3SH] + HSO_3^- \rightleftharpoons [RR'_3N^+ \cdots {}^=O_5S_2] + H_2O \qquad (7)$$

$$[RR'_3N^+ \cdots S_2O_5^=] \rightleftharpoons RR'_3N^+ + S_2O_5^= \qquad (8)$$

$$[RR'_3N^+ \cdots {}^-O_3SH] + RR'_3N^+ \rightleftharpoons [(RR'_3N)_2^+ \cdots {}^=O_3S] + H^+ \qquad (9)$$

$$[RR'_3N^+ \cdots {}^=O_5S_2] + RR'_3N^+ \rightleftharpoons [(RR'_3N)_2^+ \cdots {}^=O_5S_2] \qquad (10)$$

where $RR'_3N^+$ represents the CTAB cation. So bisulfite becomes highly susceptible to oxidation through the complexation between CTAB micelles and bisulfite ion species, i.e. the bisulfite ion species complex ought to be the most active species.

Reaction (2) becomes more complicated with respect to the reaction path by which the bisulfite ion species complex can effectively participate in the one-electron transfer reaction with monomer in the presence of CTAB micelles. The cause of the pronounced rise in $R_p$ at $[CTAB] = 8.0 \times 10^{-3}$ M, the second CMC, can be explained in terms of micellar interaction. One possible role of the micellar effect is that the rate enhancement is affected by a high local concentration of CTAB-bound bisulfite ion species on the rod-like micellar surface which has large aggregation numbers. The high $R_p$ occurring in the concentration of the second CMC of CTAB indicates that the reaction rates are sensitive to the changes in micellar structure.

### *Polymerization of acrylamide in microemulsions*

*Effect of microemulsion structures on polymerization rate.* *Figure 4* shows that the polymerization rate of acrylamide varies with the content of water at 30 and 45°C, respectively. The variations observed in *Figure 4* indicate two points, at ~27 and 56 wt% water, at which the rate of the polymerization is enhanced. Significantly, these points correspond to the transition from W/O to BC and BC to O/W (*Figure 3*). Mishra *et al.*[11] and Friberg *et al.*[10] observed such a catalysis induced by microemulsion structural transitions.

These catalyses in micellar and microemulsion structural transitions in the present studies showed that the structural transitions can catalyse reactions, and the rate of polymerization of acrylamide can be enhanced at the micellar and microemulsion structure transition points. No suitable theory exists for explaining these observation up to now. But there have been attempts to connect the critical point of a system to the reaction rate[23], and we will study the connection further in the future.

*Effect of microemulsion structure on polyacrylamide molecular weights.* The molecular weights of polyacrylamide in the different microemulsion media were determined by viscosity measurements at 30°C. The microemulsion composition for 1, 2, 3 and 4 is the ratio of $W_{CTAB}:W_{n\text{-octane}}:W_{water} = 9:2:9$, and the contents of n-butanol decrease in proper order. The microemulsion composition for 5, 6, 7 and 8 are $W_{CTAB}:W_{n\text{-octane}}:W_{n\text{-butanol}} = 9:2:9$, and the contents of water increase in proper order. 1, 2, 3 and 4 are W/O microemulsion media; 5, 6 and 7 are BC microemulsion media, and 8 and 9 are O/W microemulsion media. The results are listed in *Table 1*.

**Table 1** Effect of microemulsion structures on polyacrylamide molecular weights at 30°C; [acrylamide]/[bisulfite] is constant

| | W/O | | | | BC | | | O/W | |
|---|---|---|---|---|---|---|---|---|---|
| Microemulsion composition | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| $M \times 10^{-5}$ | 6.58 | 9.65 | 9.58 | 7.34 | 5.75 | 3.68 | 2.92 | 5.60 | 4.57 |

*Figure 1* and *Table 1* show that the molecular weights of polyacrylamide are different in different microemulsion media. The highest molecular weights are obtained in W/O microemulsion media because polyacrylamide solubilized in W/O microemulsion media; the lowest are obtained in BC because they were stopped easily by the free-radical reaction; and the highest are obtained in O/W. So microemulsions were shown to be suitable as a medium for the production of polyacrylamide in which molecular weights can be controlled and predicted by variations in microemulsion structures.

## ACKNOWLEDGEMENT

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