

Polymerization of Acrylamide in a Micellar Medium: Inhibition Effect of Surfactants

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ABSTRACT: The polymerization of acrylamide (AM) in an aqueous medium and in the presence of anionic [sodium lauryl sulfates (NaLS)], cationic [cetyltrimethyl ammonium bromide (CTAB)], and nonionic (Brij-35) surfactants was carried out at 60°C with potassium persulfate as the initiator. The percentage conversion and rate of polymerization (R_p) decreased in the presence of the surfactant, and the inhibition effect of the surfactant was in the order CTAB > Brij-35 > NaLS. The viscosity data, namely, the intrinsic viscosity, viscosity-average molecular weight, and shape factor, were also obtained in

each case. The polymer was characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. The inhibition effect of the surfactant on R_p of AM was explainable on the basis of hydrophobic and electrostatic interactions during the association/binding between the surfactant and monomeric free radical of the monomer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 981–986, 2011

Key words: radical polymerization; synthesis; thermogravimetric analysis (TGA); viscosity

INTRODUCTION

Water-soluble polymers have received the considerable interest of scientists and engineers working on environmental and industrial problems. The most important synthetic polymer is polyacrylamide (PAM),¹ which has many applications² in the fields of chemicals, mineral processing, water treatment, and so on. PAM was first synthesized by Riggs and Rodriguez^{3,4} with potassium persulfate as an initiator by the dilatometer technique. A series of comprehensive studies⁵ was made to elucidate the reaction mechanism for the polymerization of acrylamide (AM) in aqueous media.

The polymerization of AM in a micellar medium has received the attention of various research groups. The polymerization of AM in aqueous surfactant solutions, initiated by potassium persulfate, has been studied.⁶ Below the critical micelle concentration (cmc), cationic, anionic, and nonionic surfactants had no effect, whereas above the cmc, only cationic soaps had an effect, decreasing the rate of polymerization (R_p) and molecular weight. The results of the polymerization of AM in mixed micellar solutions of surfactants, namely, mixed micellar systems of cationic or anionic with zwitterionic sur-

factants and cationic with nonionic surfactants have shown⁷ a catalytic effect of surfactant systems on the polymerization. However, a nonionic (Brij-35)/anionic [sodium lauryl sulfate (NaLS)] mixed micellar system had an inhibition effect on R_p . These effects were attributed to the effect of the Stern layer of mixed micelles on the step of the initiator to form free radicals.

The kinetics of polymerization of AM with KMnO_4 -cyclohexane and Cr(VI) -cyclohexane redox systems as initiators in the presence of surfactants have also been investigated.^{8,9} The anionic surfactant, sodium dodecyl sulfate, above its cmc enhanced R_p . However, the presence of a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), decreased R_p , whereas a nonionic surfactant (Triton X-100) had no effect on R_p . The kinetics of polymerization of AM initiated by potassium peroxidizulfate in water was studied¹⁰ in the presence of an anion-active emulsifier, sodium dodecylphenoxy benzene disulfonate. The emulsifier was found to affect the relative molecular mass of PAM, but it showed no effect on R_p .

During the emulsion copolymerization¹¹ of acrylonitrile and butyl acrylate initiated by $\text{K}_2\text{S}_2\text{O}_8$ in the presence of anionic, cationic, and nonionic emulsifiers at 60°C, it was observed that R_p , in the range of 15–70% conversion, was proportional to 0.41, 0.48, and –0.42 powers of the emulsifier concentration of the anionic, nonionic, and cationic emulsifiers, respectively. The exponent of the emulsifier concentration decreased with increasing

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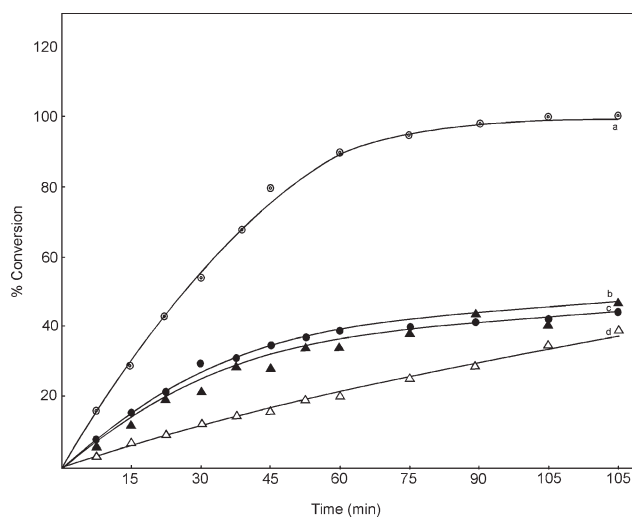


Figure 1 Percentage conversion versus time at 60°C: (a) in the absence of surfactant, (b) in the presence of NaLS, (c) in the presence of Brij-35, and (d) in the presence of CTAB.

emulsifier concentration in the case of the anionic and nonionic emulsifiers. The unexpected polymerization behavior in the presence of the cationic emulsifier was explained by the formation of a product due to interaction of the initiator with the emulsifier.

In this investigation, we studied the polymerization of AM in an aqueous micellar medium, that is, in the presence of an anionic surfactant (NaLS), cationic surfactant (CTAB), and nonionic surfactant (Brij-35). The percentage conversion, R_p , molecular weight, and viscosity data of the synthesized PAM in the presence of the three surfactants were evaluated and are discussed.

EXPERIMENTAL

Materials

AM (obtained from E. Merck, Mumbai, India) was purified by the methods reported by Dainton and Tordoff.¹² The initiator, potassium persulfate, was analytical grade (Thomas Baker, Mumbai, India) and was not purified further. The surfactants, namely, NaLS (Thomas Baker), CTAB (Thomas Baker), and Brij-35 (Thomas Baker) were used as received. However, their cmc values were checked by surface tension measurement and were found to be 8.2×10^{-3} , 9.7×10^{-4} , and 9.0×10^{-5} mol/dm³, respectively, at 25°C. These observed values of cmc were in close agreement with the reported values^{13–15} of cmc, that is, 8.0×10^{-3} , 9.8×10^{-4} , and 9.2×10^{-5} mol/dm³ at 25°C for NaLS, CTAB, and Brij-35, respectively. All of the other reagents were analytical grade. Double-distilled deionized water was used as the solvent. Freshly prepared solutions of surfactant were used to prevent aging.

Procedure

We used the gravimetric technique, that is, the conversion of the monomer to polymer by stopping polymerization and isolating and weighing the resulting polymer, to study the polymerization. The requisite quantity of purified monomer, surfactant, and water were mixed in the reaction vessel (vessel fitted with a B_{24/29} socket carrying a B_{24/29} cone with inlet and outlet tubes), and N₂ gas was passed for the removal of dissolved oxygen. The reaction vessel was thermostated in an oil bath at the desired temperature (60°C) with accuracy of $\pm 1^\circ\text{C}$ for about 15 min. The required amount of potassium persulfate, kept at the same temperature in a separate flask, was added to the reaction vessel, and the polymerization was allowed¹⁶ to proceed with continuous stirring of the reaction mixture. After the specified time interval, the polymer solution was poured into a beaker containing cold methanol (twice the volume of the polymer solution); then, the mixture was stirred continuously. The polymer formed was washed repeatedly with conductivity water and dried to a constant weight.

The percentage conversion were calculated with the following formula:

$$\text{Conversion (\%)} = \frac{\text{Weight of the polymer}}{\text{Weight of the monomer}} \times 100$$

R_p was obtained with the help of the slope of the linear portion of the curve plotted between the percentage conversion and time for polymerization up to 40% only (Fig. 1).

Viscosity measurement

The intrinsic viscosity $[\eta]$ of the polymers, expressed in deciliters per gram, was measured in an aqueous solution at $25 \pm 1^\circ\text{C}$ with an Oswald viscometer (Kanpur, India). The viscosity-average molecular weight (M_v) was calculated with the Mark–Houwink equation:

$$[\eta] = KM^\alpha$$

where the values¹⁷ of K and α were 6.8×10^{-4} and 0.66, respectively, at 25°C.

Thermogravimetric analysis (TGA)

TGA was done with a thermogravimetric analyzer (TGA Q50V20 TA, USA) in a nitrogen atmosphere at a heating rate of 10°C/min. Powdered sample (5 ± 1 mg) was used in each case.

TABLE I
 R_p at 60°C in the Absence and Presence of Surfactants

PAM	$R_p \times 10^4$ (mol dm ⁻³ s ⁻¹)
In the absence of surfactant	3.33
In the presence of NaLS	1.88
In the presence of CTAB	0.78
In the presence of Brij-35	1.55

IR analysis

The IR spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (Bruker Vector 22) with KBr pellets.

RESULTS AND DISCUSSION

Characterization of the polymer

IR spectra

FTIR spectra of the synthesized PAM were recorded in each case, that is, in aqueous medium and in the presence of NaLS, CTAB, and Brij-35 and were computerized with the reported¹⁸ FTIR spectra of PAM synthesized in the absence of surfactant. Each spectra showed the characteristic peaks of PAM. The broad peaks were observed at 3443 cm⁻¹ due to -NH stretching vibration, between 2924 and 2855 cm⁻¹ due to -CH stretching, at 1631 cm⁻¹ due to C=O stretching, at 2924 cm⁻¹ due to -CH₃ vibration, between 1383 and 1460 cm⁻¹ due to -CN stretching, at 1105 cm⁻¹ due to a -C-C- asymmetric trend, and at 797-800 cm⁻¹ due to -N-H, which was out of plane. These data (spectra) showed that a similar stretching compound (PAM) was synthesized in each case. However, in case of PAM synthesized in the presence of Brij-35 (nonionic surfactant), the intensity changed at 1087 cm⁻¹ because of the hydrogen-bond character of Brij-35.

TGA

The thermogravimetric study of PAM showed¹⁹ that water, ammonia, and a small quantity of CO₂ are released in the first decomposition in the temperature range 220-340°C, where the polymer chains remain intact. The reaction occurs on the pendant amide group in the second stage of decomposition in the temperature range 340-440°C, where the major weight loss occurs with main-chain breakdown and gives CO₂, water, nitrile compounds, and imides. In this investigation, TGA of the polymers synthesized in the absence and presence of the surfactants, namely, NaLS, CTAB, and Brij-35 was carried out. The percentage weight loss in the temperature range 400-420°C in polymers synthesized in the absence and presence of NaLS, CTAB, and

Brij-35 were obtained as 56 ± 2, 55 ± 2, 35 ± 3, and 50 ± 3%, respectively. These data clearly indicate that the polymer (PAM) synthesized in the presence of CTAB was more stable. The polymers synthesized in the aqueous medium or in the NaLS/Brij-35 micellar medium had almost same stability but less than that of the polymer synthesized in the presence of CTAB.

Percentage conversion and R_p

The polymerization of AM in water with potassium persulfate as the initiator was already studied in detail.²⁰ R_p may be expressed as

$$R_p \propto (K_2S_2O_8)^{0.5} (AM)^{1.25 \pm 0.05}$$

An insignificant effect of pH on R_p was also observed. Similar results were observed during this investigation and, therefore, are not given in this communication. Only the effect of the surfactants on the polymerization are discussed. The percentage conversion versus time plots at 60°C for the polymerization of AM in the absence and presence of NaLS, CTAB, and Brij-35 are given in Figure 1, which shows that the monomer conversion rate was very fast in the early stage of polymerization, and all of the curves in Figure 1 show the same trend. Also, in 2 h, the percentage conversion in the presence of CTAB was 30-40% only, and the polymerization process proceeded at a smooth rate (Fig. 1).

However, the percentage conversion decreased in the presence of surfactant in each case. The maximum decrease in the percentage conversion was observed in the presence of the cationic surfactant (CTAB). R_p was obtained through consideration of the percentage conversion up to 40% only. R_p also decreased in the presence of the surfactants (Table I).

Viscosity data of the polymer (PAM)

The viscosity data of the synthesized polymer (PAM) in the absence and presence of the surfactants were determined. The relative viscosity (η_{rel}) and specific viscosity (η_{sp}) increased with decreasing polymer concentration (C) in each case (Table II). $[\eta]$ was obtained from the plot of η_{sp}/c versus C (Fig. 2) and $(\ln \eta_{rel})/c$ versus C (Fig. 2) and from the extrapolation of the plot at $c = 0$. The value of $[\eta]$ was found to be the same (Table II) from both of the plots. M_v was calculated for the polymers synthesized in the absence and presence of the surfactants. The values of $[\eta]$ and M_v of the polymer were almost same when it was synthesized in the absence and presence of the nonionic surfactant (Brij-35). However, the values of $[\eta]$ and M_v of the polymer synthesized in the presence of NaLS or CTAB were

TABLE II
Viscosity Data of the Polymer Synthesized in the Absence and Presence of Surfactants

	PAM % (w/v)	η_{rel}	η_{sp}	η_{sp}/C	$\ln \eta_{rel}/C$	$[\eta]$	Molecular weight
In the absence of surfactant	0.25	1.60	0.60	2.40	1.88		
	0.50	2.50	1.50	3.00	1.83		
	0.75	3.40	2.40	3.21	1.65	1.9 ± 0.1	1.65×10^5
	1.00	5.00	4.00	4.00	1.60		
NaLS	0.25	1.90	0.90	3.60	2.56		
	0.50	3.20	2.30	4.60	2.38	2.6 ± 0.1	2.36×10^5
	0.75	5.28	4.28	5.71	2.21		
	1.00	7.85	6.85	6.85	2.06		
CTAB	0.25	2.10	1.10	4.37	2.94		
	0.50	4.28	3.28	6.56	2.90		
	0.75	7.92	6.92	9.22	2.75	3.2 ± 0.1	2.51×10^5
	1.00	11.50	10.50	10.50	2.44		
Brij-35	0.25	1.76	0.76	3.04	2.26		
	0.50	2.93	1.93	3.87	2.15	2.1 ± 0.1	1.52×10^5
	0.75	5.00	4.00	5.33	2.14		
	1.00	7.00	6.00	6.00	1.94		

found to increase. The polymer synthesized in the presence of CTAB had maximum values of $[\eta]$ and M_v .

The η_{rel} data at different Cs were also used to calculate the voluminosity (V_E) of the polymer solutions at given temperatures. We determined V_E plotting $Y^{21,22}$ against C (w/v %), where Y is given as

$$Y = (\eta_{rel}^{0.5} - 1) / C(\eta_{rel}^{0.5} - 0.1)$$

A plot of Y versus C (% w/v; Fig. 3) gave a straight line, which, on extrapolation to $C = 0$, gave

an intercept. V_E was determined from the intercept in each case and is given in Table III.

The shape factor, which gives an idea about the polymer in solution, was then calculated with the following equation:

$$[\eta] = (\text{Shape factor}) \times V_E$$

The values of the shape factor^{21,22} of the polymer synthesized in the absence and presence of NaLS, CTAB, and Brij-35 are also given in

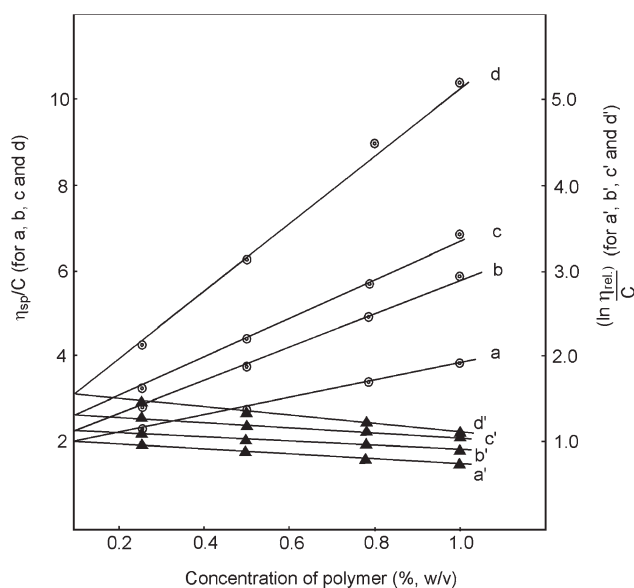


Figure 2 Plots of η_{sp}/c or $\ln \eta_{rel}/c$ versus C (w/v) at 25°C: (a) in the absence of surfactant, (b) in the presence of NaLS, (c) in the presence of Brij-35, and (d) in the presence of CTAB.

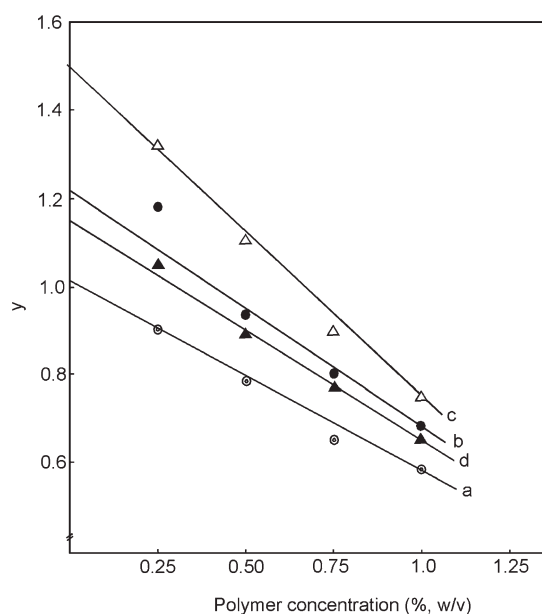


Figure 3 Plot of Y versus C (% w/v) at 25°C: (a) in the absence of surfactant, (b) in the presence of NaLS, (c) in the presence of Brij-35, and (d) in the presence of CTAB.

TABLE III
Values of γ , V_E , and Shape Factor of the Polymer
Synthesized in the Absence and Presence of Surfactants

	PAM % (w/v)	η_{rel}	γ	V_E	$[\eta]/V_E$ (shape factor)
In the absence of surfactant	0.25	1.60	0.91		
	0.50	2.50	0.78	1.01	1.88
	0.75	3.40	0.65		
	1.00	5.00	0.58		
NasLS	0.25	1.90	1.18		
	0.50	3.20	0.93	1.22	2.13
	0.75	5.28	0.78		
	1.00	7.85	0.67		
CTAB	0.25	2.10	1.33		
	0.50	4.28	1.09	1.51	2.11
	0.75	7.92	0.89		
	1.00	11.50	0.73		
Brij-35	0.25	1.76	1.06		
	0.50	2.93	0.88	1.15	1.82
	0.75	5.00	0.77		
	1.00	7.00	0.64		

Table III. The close value of the shape factor (1.9 ± 0.2) in the absence and presence of the surfactants did not indicate a variation in the spherical conformation of the macromolecules in the presence of any surfactant. The results clearly indicate the polymer with the same spherical confirmation in the absence and presence of surfactant.

One may explain the effect of the surfactant on R_p of AM by considering the mechanism of polymerization in the absence and presence of the surfactants.

In the absence of surfactant

In aqueous solution, the interaction of $S_2O_8^{2-}$ with monomer (methylacrylonitrile monomer) directly or with the water-soluble monomeric free radical was reported.²³ The most probable reactions in these experimental conditions seemed to be as given in Scheme 1.

According to Scheme 1, the rate of initiation (R_i) may be given as

$$R_i = k_i [S_2O_8^{2-}] [M] \quad (1)$$

where M is the monomer and k_i is the rate constant for initiation step(i) of scheme 1.

With bimolecular termination assumed, R_i is obtained as follows:

$$R_i = k_i^{1/2} / k_t [S_2O_8^{2-}]^{1/2} [M]^{1/2} \quad (2)$$

where k_t is the rate constant for propagation step(ii) of scheme 1

R_p is given as

$$R_p = k_p [M] R_i \quad (3)$$

where k_p is the rate constant for propagation step(ii) of scheme 1

From eqs. (2) and (3), we get

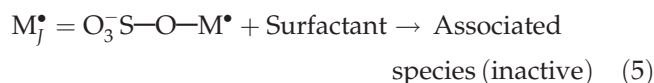
$$R_p = \left(\frac{k_i^{1/2} k_p}{k_t} \right) [S_2O_8^{2-}]^{1/2} [M]^{1/2} \quad (4)$$

The rate law [eq. (4)] was in agreement with the observed experimental results in the absence of the surfactants.

In the presence of the surfactants

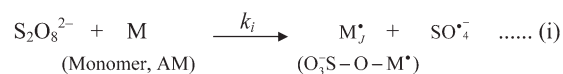
Micellar aggregation/binding is well reported^{24,25} in the literature. The electrostatic surface potential at the micellar surface can attract or repel the reaction species, and hydrophobic interactions can bring about interactions in the micelle, even of the reagent, that bear the same charge or neutral compared to the ionic micelle. Thus, the rate and mechanism of chemical reactions may be affected by means of electrostatic and/or hydrophobic interactions. The inhibition effect of the surfactants on R_p of AM could be explained by the hydrophobic and electrostatic interactions.

It seemed to be most probable that the monomer free radical ($M_j^\bullet = O_3S-O-M^\bullet$, which also had a negative charge) associated with/bound the surfactants to give an inactive species:

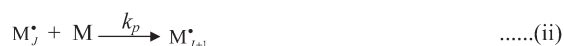


This resulted in a decrease in the concentration of M_j^\bullet in the reaction mixture, and therefore, R_p , which depended on M_j^\bullet , decreased. The hydrophobic interactions were responsible for the association/binding between the surfactants and O_3S-O-M^\bullet species, as the inhibition effect was also observed in the presence of the nonionic surfactant. The electrostatic

Initiation



Propagation



Termination



Scheme 1

interactions also became dominating in case of the ionic surfactants. In case of the anionic surfactant (NaLS), because of similar charges on the surfactant and $O_3^-S-O-M^\bullet$ species, there was repulsion between them, and this opposed association. A less observed inhibition effect of NaLS on R_p of AM was in agreement with eq. (5). However, for CTAB, which was a cationic surfactant, Eq. (5) involved interactions between oppositely charged species, and because of attractive forces, the association between the cationic surfactant and $O_3^-S-O-M^\bullet$ dominated. This resulted in the greatest inhibition effect of CTAB on R_p of AM. The results were also supported by the observed molecular weight and $[\eta]$ in the presence of the surfactants.

CONCLUSIONS

R_p of AM was found to decrease in the presence of the surfactant. The inhibition effect of the surfactants was in the order CTAB > Brij-35 > NaLS. FTIR spectroscopy, TGA, and the shape factor showed the formation of the same polymer in the absence and presence of the surfactants. The inhibition effect of the surfactant on R_p was explained by the hydrophobic and electrostatic interactions during the association between the surfactants and M_j^\bullet , which formed in the initiation step by the reaction of the monomer with $S_2O_8^{2-}$.

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