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KINETICS OF SEMIBATCH EMULSION POLYMERIZATION OF BUTYL ACRYLATE STABILIZED BY A REACTIVE SURFACTANT

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Key Words: Emulsion Polymerization, Butyl Acrylate, Reactive Surfactant, Semibatch Process, Kinetics

ABSTRACT

The monomer feed rate (R_a) is the predominant parameter for controlling the rate of polymerization (R_p) in the semibatch emulsion polymerization of butyl acrylate (BA) stabilized by a reactive surfactant, sodium dodecyl allyl sulfosuccinate (SDAS). An induction period or even a complete inhibition of the polymer reaction observed for the experiments with relatively high SDAS concentration ([SDAS]) or low initiator concentration ([I]) is attributed to intensive chain transfer of the BA radicals to SDAS. R_p increases with increasing [I], whereas, it is relatively insensitive to changes in [SDAS]. The chain transfer agent, dodecyl mercaptan (DM) or carbon bromotrichloride (CBTC), was incorporated into the monomer feed to enhance the chain transfer reaction. The consumption of DM is diffusion limited because the relatively water-insoluble DM molecules have difficulties to diffuse from the monomer droplets to the reaction loci (latex particles) and, hence, it does not show a significant effect on the reaction kinetics. On the other hand, addition of CBTC with a higher water solubility to the reaction mixture reduces R_p significantly. When R_a decreases from 6.24 to 1.04 g/min, even the reaction kinetics of the system containing CBTC becomes monomer feed rate-controlled.

INTRODUCTION

Semibatch emulsion polymerization [1-9] is a process widely used in the manufacture of latex products such as adhesives, coatings, thermoplastics, and syn-thetic rubbers. Free radical polymerization of vinyl monomers such as butyl acrylate (BA) is very exothermic and heat transfer (reaction temperature control) may become extremely difficult in a commercial scale batch reaction system. To alleviate such a problem, the semibatch process involving gradual addition of monomers into the reaction mixture can be used to effectively remove the heat released during polymerization. A latex product is a dispersion of a large number of submicron polymer particles in water. These particles are generally protected by electrostatic stabilization provided by anionic surfactants (e.g., sodium dodecyl sulfate). However, the small, mobile surfactant species can migrate toward the surface layer of the polymeric film without any difficulty. This may have a negative effect on applications such as adhesion of the pressure-sensitive adhesives. One approach to overcoming the surfactant migration problem is to introduce a reactive surfactant into the reaction system. In addition to the basic surfactant properties (e.g., lowering of surface tension and formation of micelles), the reactive surfactant can be chemically incorporated into the latex particles during polymerization. Thus, immobilized surfactant molecules are incapable of diffusing toward the surface layer of the polymeric film and deteriorating film properties.

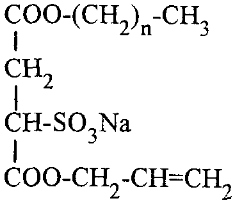
Urquiola *et al.* [10-12] used the reactive surfactant, sodium dodecyl allyl sulfosuccinate (SDAS), to prepare vinyl acetate (VA) latices in a batch reactor. It was shown that the particle size (d_p) decreases with increasing SDAS concentration ([SDAS]), that is, the number of latex particles (N_p) nucleated increases with increasing [SDAS]. Interesting enough, the rate of polymerization (R_p, which is proportional to N_p) decreases with increasing [SDAS]. This seemingly contra-dictory result was attributed to chain transfer of the VA radicals to SDAS via the α-hydrogen abstraction mechanism. The chain transfer reaction may greatly reduce the average number of free radicals per particle (n) and, thereby, lower R_p. In our previous reports, [8, 9] the authors have demonstrated how to use SDAS to prepare BA (a major component of pressure-sensitive adhesive compositions) latices with controlled d_p in a semibatch reactor and investigated the latex stability during polymerization. The objective of this project was to continue with the subject concerning the semibatch reaction kinetics. It is generally accepted that the rate of monomer addition (R_a) becomes the limiting factor in determining R_p when the system is operated under the monomer-starved condition (i.e., $R_p \geq R_a$) [2]. If chain transfer of the BA radicals to SDAS is, then the magnitude of reduction in R_p may become so large as to make the kinetics shift from the monomer feed rate-controlled to the reaction-controlled mechanism. Therefore, it is of particular interest to study whether the chain transfer reaction plays an important role in the semibatch BA emulsion polymerization using SDAS as the particle generator and stabilizer.

EXPERIMENTAL

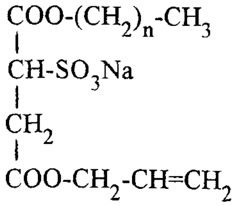
Materials

The chemicals used in this work were butyl acrylate (BA) (Formosa Plastics Co.), sodium alkyl allyl sulfosuccinate (Eleminol JS-2, Sanyo Chemical Industries), sodium persulfate (Riedel-de Haen), sodium bicarbonate (Riedel-de Haen), dodecyl mercaptan (Aldrich), carbon bromotrichloride (Aldrich), nitrogen (Ching-Feng-Harng Co.), and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance <0.057 μScm^{-1}). The monomer BA was distilled under reduced pressure before use. All other chemicals were used as received.

Eleminol JS-2 is a 50/50 mixture of the following two isomers according to the manufacturer:



$$\begin{array}{l} COO\text{-}(CH_2)_n\text{-}CH_3 \\ | \\ CH_2 \\ | \\ CH\text{-}SO_3Na \\ | \\ COO\text{-}CH_2\text{-}CH{=}CH_2 \end{array}$$



$$\begin{array}{l} COO\text{-}(CH_2)_n\text{-}CH_3 \\ | \\ CH\text{-}SO_3Na \\ | \\ CH_2 \\ | \\ COO\text{-}CH_2\text{-}CH{=}CH_2 \end{array}$$

where the value of n was determined to be 10.63 according to the elemental analysis method and the carbon-carbon double bond was confirmed by the ^{13}C-NMR spectra [8]. This indicates that the alkyl group shown above ($-(CH_2)_n-CH_3$) is dodecyl. The critical micelle concentration (CMC) of Eleminol JS-2 (SDAS) in deionized water was determined to be 6.07×10^{-4} M [8].

Polymerization Process

Semibatch emulsion polymerization was carried out in a 1-liter glass reactor equipped with a 4-bladed agitator, a thermometer, and a condenser. A typical recipe is shown in Table 1. The polymerization involves addition of water along with the surfactant and monomer to the reactor at room temperature. The initial reactor charge was purged with nitrogen for 10 minutes while the reactor temperature was

TABLE 1. Typical Recipe for Semibatch Emulsion Polymerization of Butyl Acrylate Stabilized by Reactive Surfactant SDAS

	Chemicals	Weight (g)
Monomer Feed	BA	187.10
Initial Reactor Charge	H_2O	442.24
	$NaHCO_3$	0.59
	JS-2 (38%)	12.54
	BA	9.30
Initiator Solution	H_2O	15.00
	$Na_2S_2O_8$	0.47
Total Weight		667.24
Theoretical Solid Content = 30.31%		
Monomer Feed Rate = 6.24 g/min		

brought to 70°C. The reaction was then initiated by adding the initiator solution to the reactor. After 30 minutes, the monomer was fed to the reactor over a prescribed period of time by an FMI pump. Polymerization temperature was kept constant (70 °C) throughout the reaction. After monomer feeding was complete, the reaction system was kept at 70°C for at least 30 minutes to reduce the residual monomer to an acceptable level. The theoretical solid content at the end of polymerization is around 30%.

Characterization of Latices

The latex product was filtered through a 40 mesh (0.42 mm) and a 200 mesh (0.074 mm) screen in series to collect the coagulum formed during polymerization. Scraps adhering to the agitator, thermometer, and reactor wall were also collected. The coagulum data show that the latex stability is quite satisfactory in this work. Total solid content was determined by the gravimetric method. Particle size data were obtained from the dynamic light scattering method (Otsuka Photal

LPA-3000/3100). The latex sample was diluted with water to adjust the number of photons counted per second (cps) to 8,000-12,000. The number of accumulation times was set at 50 throughout this work. The d_p data reported in this work represent an average of at least three measurements and the errors have been estimated to be 7% or less. The number of latex particles per liter reaction mixture (N_p) was calculated based on the d_p data (see Equations 1-4):

$$N_p = 6W_m(\%\ \text{monomer added}) / \{\pi d_p^3 V_t[\rho_m(1-\phi_p)+\rho_p\phi_p]\} \quad (1)$$

$$\phi_p = 1 - ([M]_p MW_m / \rho_m) \quad (2)$$

$$[M]_p = [R_a\rho_m(t-t_{imc})+W_{imc}](1-X_t)/MW_m / \{[R_a\rho_m(t-t_{imc})+W_{imc}]X_t/\rho_p + [R_a\rho_m(t-t_{imc})+W_{imc}](1-X_t)/\rho_m\} \quad (3)$$

$$X_t = W_m X / [R_a\rho_m(t-t_{imc})+W_{imc}] \quad (4)$$

where W_m is the total weight of monomer, V_t is the total volume of the finished batch, ρ_m is the monomer density (0.894 g/cm^3), ρ_p is the polymer density (1.055 g/cm^3), ϕ_p is the volume fraction of polymer in the latex particles, $[M]_p$ is the monomer concentration in the particles, and MW_m is the monomer molecular weight (128 g/mol). The parameter t is the reaction time, t_{imc} is the time for the initial monomer charge to polymerize, and W_{imc} is the weight of initial monomer charge. Note that X is the overall monomer conversion, defined as the ratio of the amount of monomer converted into polymer to the total amount of monomer in the recipe, whereas X_t is defined as the ratio of the amount of monomer converted to the amount of monomer added up to that time. Equations 3 and 4 were taken from Reference 16.

RESULTS AND DISCUSSION

Effect of Initiator Concentration

In this series of experiments, [SDAS] and R_a were kept constant at 2.43×10^{-2} M (40 times of its CMC) and 6.24 g/min (total monomer feed time = 30 minutes), respectively. The values of [SDAS] and R_a were high enough that the effect of chain transfer of the BA radicals to SDAS on R_p, if present, should be observed easily. The parameter [I] was varied from 0.05% to 0.2% based on total weight of water. Figures 1 and 2 show the effects of [I] on the X versus t and N_p versus t profiles, respectively. The solid line in Figure 1 represents the condition that monomer is converted into polymer instantaneously as soon as it has been fed to the

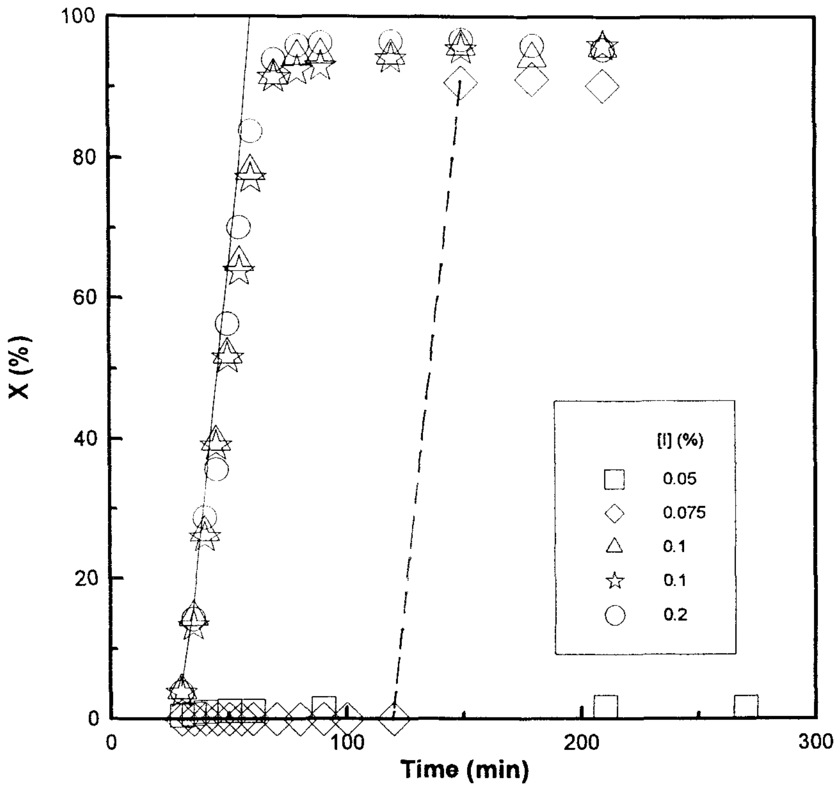


Figure 1. Effect of initiator concentration on monomer conversion versus time profiles: [I] = (□) 0.05%; (◇) 0.075%; (Δ, ☆) 0.1%; (O) 0.2%.

reactor (i.e., $R_p \geq R_a$). Other data are also compiled in Table 2, in which X_f, $d_{p,f}$, and $N_{p,f}$ represent the X, d_p, and N_p data collected at the end of polymerization. The R_p data were obtained from the relationship: $R_p = W_m$ dX/dt, in which dX/dt is the least-squares best-fitted slope of the X versus t straight line.

First, the experiment with [I] = 0.1% was carried out twice to test its reproducibility. The X versus t data in Figure 1 show that the reproducibility is satisfactory (see the triangular and starry data points). Inhibition of the polymer reaction was observed for the experiment with [I] = 0.05% and eventually no latex particles were generated throughout the reaction. For the system with a higher [I] (0.075%), an induction period of 120 minutes was observed and, consequently, almost all the added monomer was accumulated in the reactor. Subsequently, the batchwise polymerization took place rapidly, as shown by the dashed line in Figure

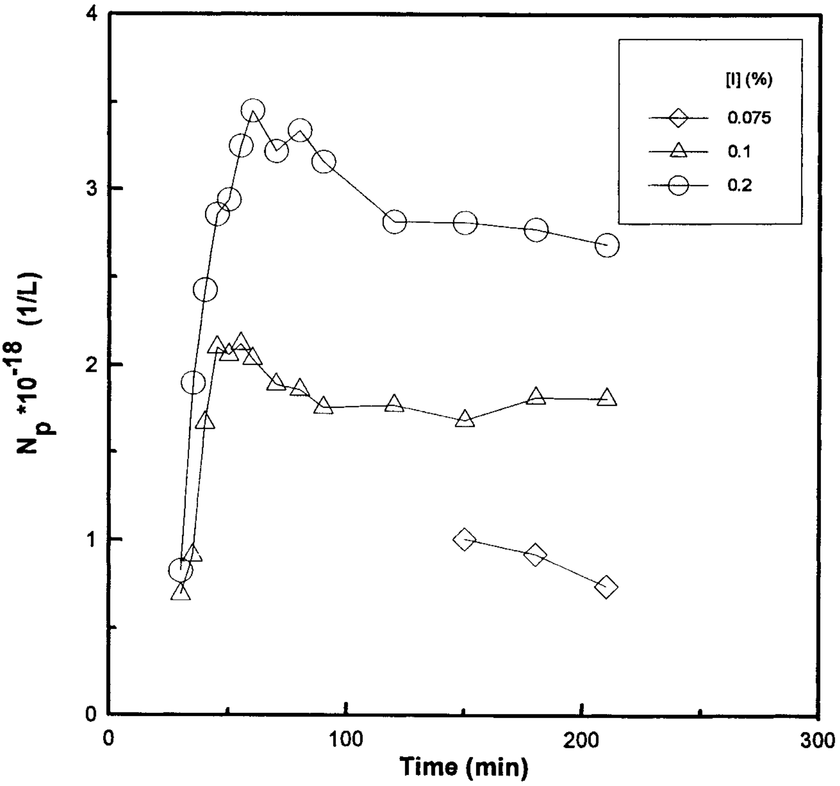


Figure 2. Effect of initiator concentration on number of particles versus time profiles: [I] = (◊) 0.075%; (Δ, ☆) 0.1%; (O) 0.2%.

1. Further increasing [I] from 0.075% to 0.1% or higher, the free radical concentration was sufficient to sustain the reaction and the system approached the monomer-starved condition (see the solid line in Figure 1). Such a trend implies that a significant fraction of the free radicals generated in water may be inactivated by chain transfer to SDAS. The resultant SDAS radicals are distributed favorably at the oil—water interface or in the aqueous phase. The SDAS radicals adsorbed on the monomer-swollen micelle surfaces or latex particle surfaces may be transferred into the aqueous phase. Transport of these SDAS radicals from the micelle surfaces into the aqueous phase may make the particle nucleation process unsuccessful. On the other hand, desorption of these SDAS radicals from the particle surfaces may reduce the average number of free radicals per particle ($\bar{n}$) (i.e., decrease R_p). As to the SDAS radicals in water, they do not contribute to the polymerization to any

TABLE 2. Experimental Data for Semibatch BA Emulsion Polymerization Stabilized by Reactive Surfactant SDAS

	X_f (%)	$d_{p,f}$ (nm)	$N_{p,f}$ x 10^{-18} (1/L)	R_p (g/min)
[I] (%)				
0.075	90.3	90.1	0.74	—
0.1 [a)]	95.8	66.7	1.81	4.87
0.2	95.5	58.5	2.69	5.32
R_a (g/min)				
6.24 [a)]	95.8	66.7	1.81	4.87
3.12	97.4	61.6	2.30	2.76
1.56	97.2	58.1	2.74	1.43
1.04	95.9	60.3	2.46	0.94
[SDAS] x10^2 (M)				
1.22	95.6	82.1	0.97	4.67
2.43 [a)]	95.8	66.7	1.81	4.87
3.65	97.1	58.3	2.71	4.87
4.86	91.7	72.6	1.42	—
Chain Transfer Agent				
None, R_a = 6.24 [a)]	95.8	66.7	1.81	4.87
DM, R_a = 6.24	96.4	75.3	1.26	4.61
CBTC, R_a = 6.24	94.7	105.0	0.46	3.67
None, R_a = 1.04	95.9	60.3	2.46	0.94
CBTC, R_a = 1.04	91.0	82.2	0.98	0.94

[a)] an average of two identical experiments

appreciable extent. It is also probable that SDAS radicals are less effective in reinitiating the polymerization as compared to the initiator radicals. All these factors may cause a significant decrease in R_p.

As shown in Table 2, the value of R_p for the system with [I] = 0.2% is slightly larger than that for the system with [I] = 0.1%. This is primarily due to the fact that $d_{p,f}$ decreases with increasing [I], that is, the number of reaction loci (N_p)

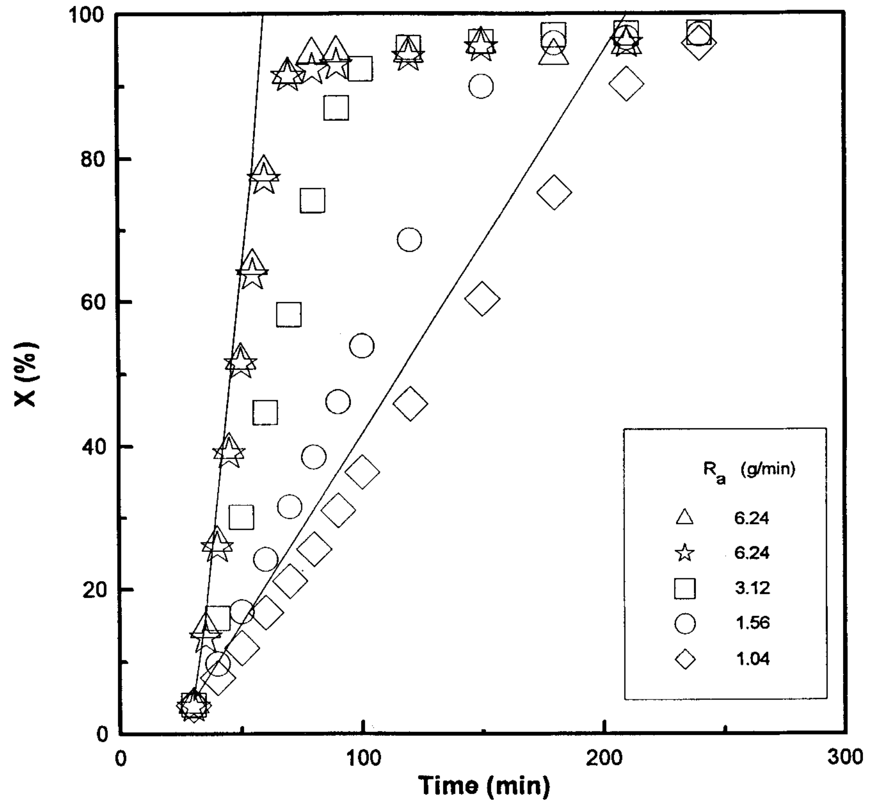


Figure 3. Effect of monomer feed rate on monomer conversion versus time profiles: R_a = (Δ, ☆) 6.24; (□) 3.12; (O) 1.56; (◊) 1.04 g/min.

nucleated increases with increasing [I] (see Figure 2 and Table 2). The larger the number of reaction loci available for consumption of the imbibed monomer, the faster is the rate of polymerization. The increased flux of free radicals toward the latex particles also contributes to the faster R_p when [I] increases from 0.1% to 0.2%. It should be noted that N_p first increases rapidly and then levels off as the polymerization proceeds. This is most likely due to the continuous particle nucleation in the presence of high levels of SDAS.

Effect of Monomer Feed Rate

In this series of experiments, [SDAS] and [I] were kept constant at 2.43×10^{-2} M (40 times of its CMC) and 0.1%, respectively. R_a was varied from 1.04 to 6.24 g/min (the corresponding monomer feed time was varied from 180 to 30 min). Figures 3 and 4 show the effects of R_a on the X versus t and N_p versus t

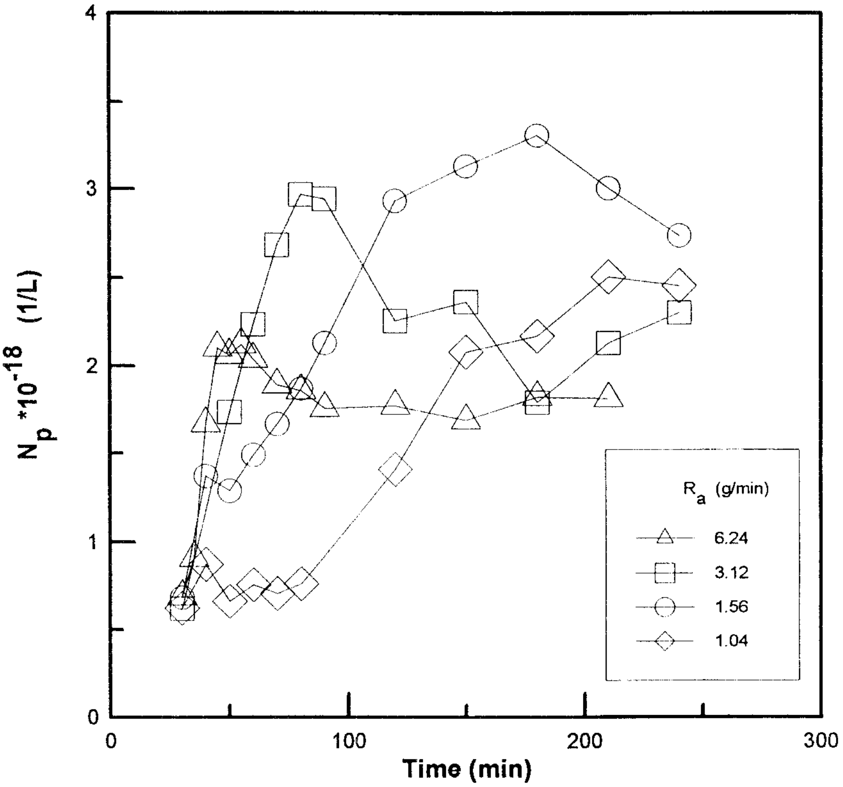


Figure 4. Effect of monomer feed rate on number of particles versus time profiles: R_a = (Δ, ☆) 6.24; (□) 3.12; (○) 1.56; (◊) 1.04 g/min.

profiles, respectively. The two solid lines in Figure 3 represent the condition that $R_p \geqq R_a$ for the system with R_a equal to 6.24 and 1.04 g/min, respectively. As shown in Table 2, $d_{p,f}$ seems to decrease slightly with decreasing R_a, that is, $N_{p,f}$ increases with decreasing R_a. Note that R_p is proportional to N_p. In this series of polymerizations, however, R_p decreases significantly with decreasing R_a, as shown in Figure 3 and Table 2. This result implies that the reaction kinetics is monomer feed rate-controlled within the range of R_a studied.

Wessling [2] analyzed the kinetics of semibatch emulsion polymerization and predicted that the system which follows Smith-Ewart case II kinetics [13-15] will approach a pseudo-steady state if R_a remains constant. In the pseudo-steady state, R_p is dependent on R_a according to the following equation:

$$1 / R_p = 1 / K + 1 / R_a \qquad (5)$$

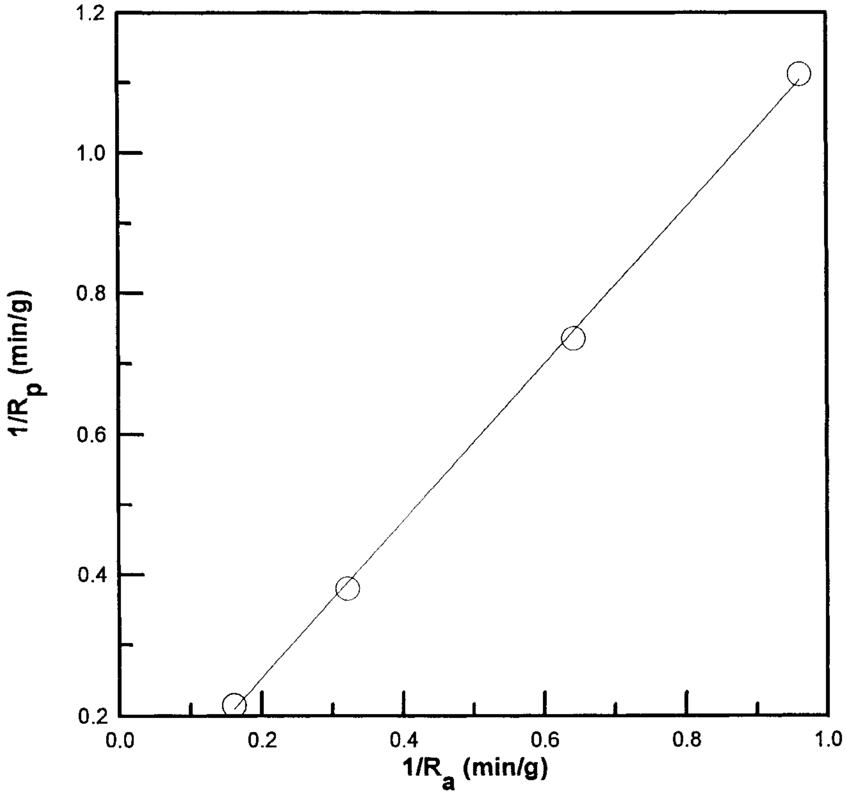


Figure 5. Reciprocal of polymerization rate as a function of reciprocal of monomer feed rate: [SDAS] = 2.43×10^{-2} M and [I] = 0.1%.

where $K = K_pN_p\,\bar{n}/(N_aV_m)$. The parameter K_p is the propagation rate constant (6.42×10^{3} L/mol-min [17]), N_a is Avogadro's number, and V_m is the molar volume of monomer (0.143 L/mol). Thus, the plot of $1/R_p$ versus $1/R_a$ data should result in a straight line with a slope of unity and an intercept of $1/K$.

As shown in Figure 5, the reaction system with various values of R_a follows Equation 5 reasonably well. The resultant slope and $1/K$ is 1.12 (slightly larger than the theoretical value) and 5.84×10^{-3} L-min/mol, respectively. This result further supports that R_a is the predominant factor in determining R_p, even though the chain transfer reaction between the BA radicals and SDAS may take place during polymerization. From the intercept, the product of $N_p\bar{n}$ was determined to be 5.86×10^{18} 1/L. If the average value of the $N_{p,f}$ data (2.33×10^{18} 1/L) was used for this series of experiments with various levels of R_a, then the average value of $\bar{n}$ was estimated to be at least 2.5. This is reasonable since the system was operated near

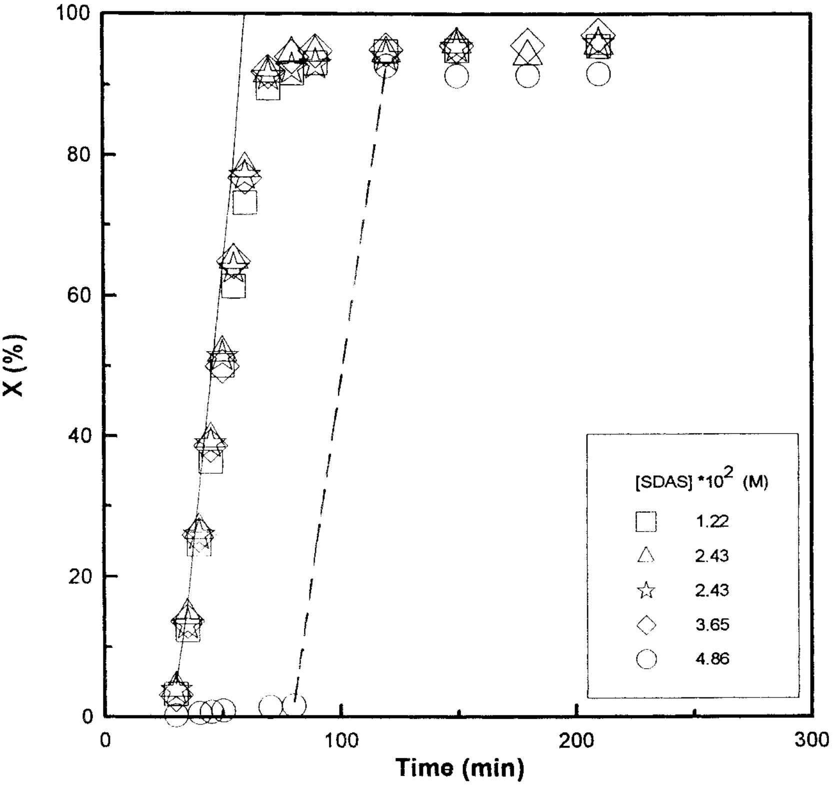


Figure 6. Effect of reactive surfactant concentration on monomer conversion versus time profiles: [SDAS] = (□) $1.22\text{x}10^{-2}$; (△, ☆) $2.43\text{x}10^{-2}$; (◇) $3.65\text{x}10^{-2}$; (○) $4.86\text{x}10^{-2}$ M.

the monomer-starved condition and termination between two encountered polymeric radicals might become diffusion-controlled due to the very high viscosity in the latex particles [6]. As a consequence, the termination reaction is retarded severely and the free radical concentration in the particles may build up rapidly during the monomer addition period. Note that the chain transfer reaction is expected to lower $\bar{n}$ because the resultant SDAS radicals may desorb from the particle surfaces. Furthermore, the greatly retarded termination reaction may also result in an increase in the molecular weight of polymer produced and for emulsion polymerization of acrylic monomers some polymer gel may even form during polymerization at this level of $\bar{n}$. This factor will override the influence of the chain transfer reaction between the polymeric radicals and SDAS, which will reduce the polymer molecular weight instead. Thus, the chain transfer reaction cannot be ruled out simply based on the condition that n is much greater than 0.5 because of the dominant effect of R_a.

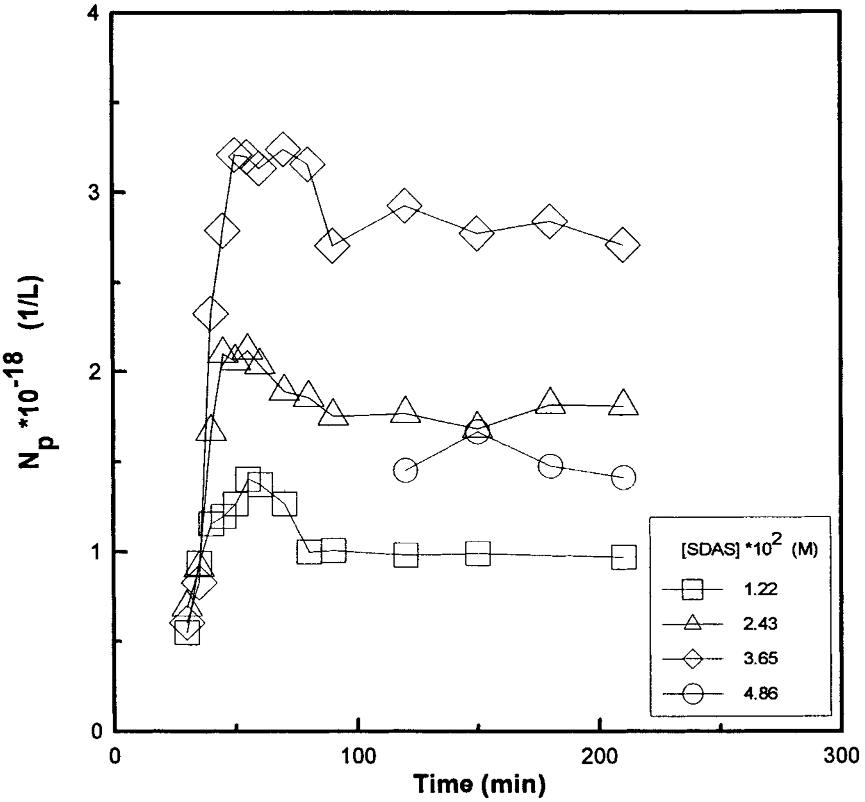


Figure 7. Effect of reactive surfactant concentration on number of particles versus time profiles: [SDAS] = (□) 1.22×10^{-2}; (Δ) 2.43×10^{-2}; (◊) 3.65×10^{-2}; (○) 4.86×10^{-2} M.

Effect of SDAS Concentration

In this series of experiments, [I] and R_a were kept constant at 0.1% and 6.24 g/min, respectively. The parameter [SDAS] was varied from 1.22×10^{-2} (20 times of CMC) to 4.86×10^{-2} M (80 times of CMC). Figures 6 and 7 show the effects of [SDAS] on the X versus t and N_p versus t profiles, respectively. As expected, d_p decreases and N_p increases with increasing [SDAS] except the experiment with the highest [SDAS] (4.86×10^{-2} M) (see Figure 7 and Table 2). However, R_p seems to be insensitive to changes in [SDAS] except the experiment with [SDAS] = 4.86×10^{-2} M (see Figure 6 and Table 2). It is then postulated that the effect of the increased N_p is counterbalanced by the opposite effect of the increased chain transfer of the BA radicals to SDAS when [SDAS] increases from 1.22×10^{-2} to 3.65×10^{-2} M. Another possible explanation is that R_p is strongly dependent on R_a and this factor makes the reaction kinetics less sensitive to changes in [SDAS].

For the system with [SDAS] = 4.86x10^{-2} M and [I] = 0.1%, a retardation period of 80 minutes was observed and, thereafter, the batchwise polymerization took place rapidly, as shown by the dashed line in Figure 6. This behavior is quite similar to the system with [SDAS] = 2.43x10^{-2} M and [I] = 0.075% (see the diamond data points in Figure 1). These data suggest that SDAS may retard the semibatch BA emulsion polymerization. This is probably due to the scenario that chain transfer of the BA radicals to SDAS produces the surface active SDAS radicals which may desorb from the latex particle surfaces or reinitiate the polymer reaction less effectively. As a result, the effective concentration of free radicals in the latex particles (reaction loci) is greatly reduced and a retardation period is observed. Another possible explanation is that the impurity present in the SDAS species may deplete the oligomeric radicals generated in water and cause retardation in the polymerization.

Effect of Chain Transfer Agent

The above kinetic data provide evidence of chain transfer of the BA radicals to SDAS. It was postulated that intensive chain transfer reaction may cause an induction period followed by a rapid polymerization or may even result in a complete inhibition of the polymerization for the experiments with higher levels of [SDAS] and/or lower [I]. Unfortunately, it has been very difficult to detect the minute differences in the X versus t data originating from the chain transfer reaction over a wide range of experimental conditions. This is due to the nature of the semibatch process, that is, R_a plays an important role in the reaction kinetics. In an attempt to demonstrate the effect of the chain transfer reaction, a more effective chain transfer agent (CTA) such as dodecyl mercaptan (DM) or carbon bromotrichloride (CBTC) was incorporated into the monomer feed. In this series of polymerizations, [SDAS] and [I] were kept constant at 4.86x10^{-2} M and 0.1%, respectively. The polymerization in the absence of CTA was chosen as the reference (see the triangular and starry data points in Figure 8 and the triangular data points in Figure 9).

Figures 8 and 9 show the effects of DM or CBTC on the X versus t and N_p versus t profiles, respectively. The X_f, $d_{p,f}$, $N_{p,f}$, and R_p data are listed in Table 2. Incorporation of DM into the monomer feed leads to an increase in $d_{p,f}$ and a decrease in both $N_{p,f}$ and R_p as compared to the reference at R_a = 6.24 g/min. However, the differences between the experiment with DM and the reference are not

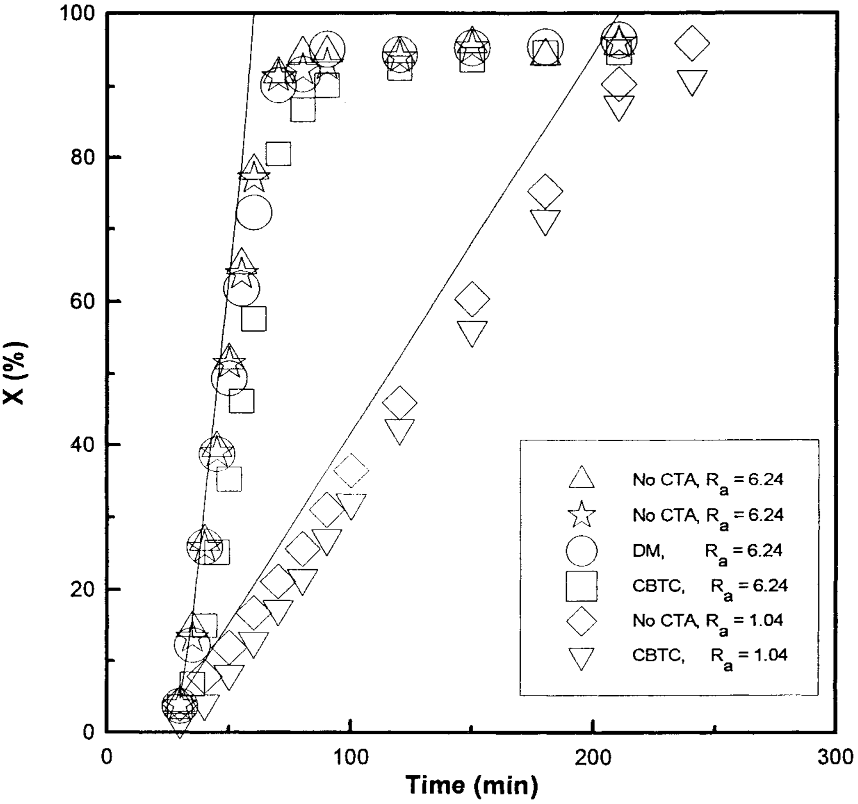


Figure 8. Effect of added chain transfer agents (CTA) on monomer conversion versus time profiles: (Δ, ☆) no CTA, R_a = 6.24 g/min; (○) DM, R_a = 6.24 g/min; (□) CBTC, R_a = 6.24 g/min; (◊) no CTA, R_a = 1.04 g/min; (∇) CBTC, R_a = 1.04 g/min.

significant, as shown in Figs 8 and 9 and Table 2. On the other hand, $d_{p,f}$ increases from 66.7 to 105.0 nm, $N_{p,f}$ decreases from 1.81x10^{18} to 4.60x10^{17} 1/L, and R_p decreases from 4.87 to 3.67 g/min when CBTC is used as the CTA. The chain transfer constants (C_s) for the styrene radicals to carbon tetrachloride, carbon tetrabromide, and DM are 0.011, 2.2, and 20, respectively. The values of C_s for the first two CTAs were taken from Reference 18 and that for DM was reported in Reference 19. Judging from these C_s data, the rate of chain transfer of the BA radicals to DM should be much faster than that of the BA radicals to CBTC. The contradiction that DM is less effective in reducing R_p than CBTC can be attributed to their different water solubilities. The long chain mercaptan (DM) is relatively

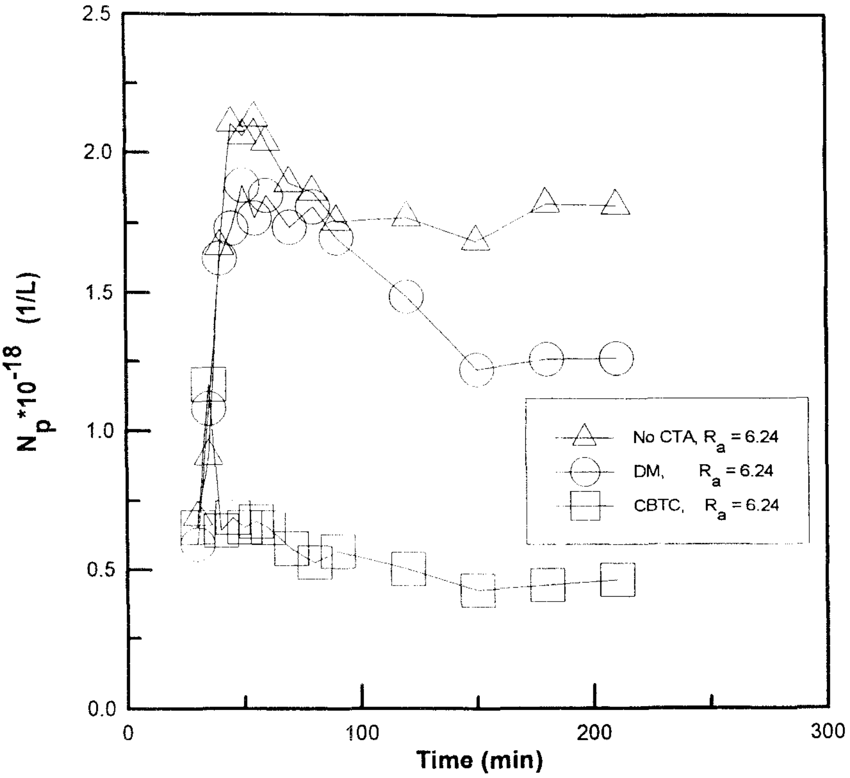


Figure 9. Effect of added chain transfer agents on number of particles versus time profiles: (Δ) no CTA, R_a = 6.24 g/min; (O) DM, R_a = 6.24 g/min; (□) CBTC, R_a = 6.24 g/min.

water-insoluble (water solubility = $3x10^{-5}$ M [20]) and, therefore, it is extremely difficult for DM to diffuse from the monomer droplets to the reaction loci (latex particles). Thus, the effective concentration of DM in the latex particles is low and the influence of the chain transfer reaction on the reaction kinetics is rather limited. On the other hand, mass transfer of CBTC with a higher water solubility (water solubility~$1x10^{-2}$ M) through the aqueous phase to the particle phase should not be a severe problem, as reflected by the greatly reduced R_p. This result is consistent with the work of Lee and Poehlein [21]. Indeed, the influence of the chain transfer reaction involving an effective CTA (e.g., CBTC) and a faster R_a (e.g., 6.24 g/min) can be observed clearly.

For the CBTC containing system at R_a = 1.04 g/min, $d_{p,f}$ increases from 60.3 to 82.2 nm and $N_{p,f}$ decreases from $2.46x10^{18}$ to $9.80x10^{17}$ 1/L in comparison with the reference. This trend is similar to that observed for the series of experiments with R_a = 6.24 g/min. Chain transfer of the incoming BA radicals to CBTC in the micelles results in CBTC radicals. These small, mobile CBTC radicals have a great chance to escape from the micelles before they can reinitiate the polymer reaction and convert these micelles into the latex particles. As a result, N_p decreases significantly in comparison with the reference (see Figure 9 and Table 2). When the chain transfer reaction takes place in the growing latex particles, the resultant CBTC radicals may also desorb from the reaction loci. This event will cause a decrease in $\bar{n}$ and, thereby, lower R_p. Nevertherless, the experimental data show that R_p remains constant (0.94 g/min) even when the very effective CBTC is used as the CTA in the semibatch BA emulsion polymerization. This is simply because the reaction kinetics becomes monomer feed rate-controlled at such a low R_a.

The results obtained from this work suggest that a simple batch reaction system may be the best candidate for investigating the influence of SDAS on the reaction kinetics of BA emulsion polymerization. It is of great interest to quantitatively study the role of SDAS in the particle nucleation and growth process. Experimental work on the batch BA emulsion polymerization stabilized by SDAS is in progress in our laboratory.

CONCLUSION

In the semibatch emulsion polymerization of butyl acrylate (BA) stabilized by a reactive surfactant, sodium dodecyl allyl sulfosuccinate (SDAS), the monomer feed rate (R_a) is the most important reaction parameter for controlling the rate of polymerization (R_p). The plot of $1/R_p$ versus $1/R_a$ data is linear with a slope close to unity, which is consistent with the simple equation developed by Wessling. The average number of free radicals per particle was estimated to be at least 2.5 during the monomer addition period. This is due to the diffusion-controlled termination reaction occurring in the semibatch reaction system operated under the monomer-starved condition. An induction period or even a complete inhibition of the polymer reaction observed for the experiments with relatively high SDAS concentration ([SDAS]) or low initiator concentration ([I]) can be attributed to intensive chain transfer of the BA radicals to SDAS, presumably via the α–hydrogen abstraction mechanism. As expected, R_p increases with increasing [I]. R_p is relatively insensitive to changes in [SDAS], even though the number of latex particles (N_p) increases with increasing [SDAS] ($R_p \sim N_p$).

The chain transfer agent (CTA), dodecyl mercaptan (DM) or carbon bromotrichloride (CBTC), was incorporated into the monomer feed to study the influence of the chain transfer reaction on the reaction kinetics. The polymerization in the absence of CTA was used as the reference. First, R_a was kept constant at 6.24 g/min. The consumption of DM is diffusion limited because the relatively water-insoluble DM molecules have difficulties to diffuse from the monomer droplets to the latex particles and, hence, the effective concentration of DM in the latex particles is quite low. As a result, DM does not show a significant effect on the reaction kinetics. On the other hand, transport of CBTC with a higher water solubility from the monomer droplets to the latex particles should not be a problem, as shown by the greatly reduced R_p. When R_a decreases from 6.24 to 1.04 g/min, even the CBTC containing system becomes monomer feed rate-controlled.

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