

Semibatch Emulsion Polymerization of Butyl Acrylate. II. Effects of Emulsifier Distribution

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ABSTRACT: The effects of emulsifier distribution ratio between the initial charge and the feed on particle formation and kinetics of butyl acrylate emulsion polymerization, using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator, were investigated. The number of particles increased with initial emulsifier concentration in the reactor charge. It was shown that traditional ranking, in terms of number of particles produced, of semibatch emulsion polymerization with monomer emulsion feed is not always justified and a semibatch emulsion polymerization can produce far more particles than a conventional batch emulsion polymerization. The number of polymer particles was found to be practically independent of the emulsifier distribution ratio between the charge and the feed for a high overall emulsifier concentration, while for a low overall emulsifier concentration, the number of particles increased with initial loading of the emulsifier. The polydispersity index (PDI) of the final latexes showed a minimum with emulsifier distribution. A bimodal particle size distribution, and a latex with a large PDI, was obtained when there was no emulsifier in the charge. As the initial emulsifier charge increased, a unimodal PSD with a smaller PDI was obtained. With higher proportions of emulsifier in the initial charge, the PDI rose again due to particle nucleation at monomer-starved conditions, and a skewed unimodal PSD was obtained. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 582–597, 2001

Key words: semibatch emulsion polymerization; butyl acrylate; emulsifier distribution; particle number; surface tension

INTRODUCTION

Semibatch emulsion polymerization processes are being used widely for the production of many varieties of commercial commodities, and for high value-added specialities, due to their flexibility in product design, and process control.¹ Such flexibility is acquired by adopting different start-up procedures. The start-up procedures for semibatch processes with monomer emulsion (ME) feed can significantly change the number of par-

ticles and particle size distribution (PSD). The distribution of reaction ingredients between the initial reactor charge and the feed is the main variable in start-up policies. The simplest case for study is when the whole recipe, including all ingredients, is divided into two parts: initial charge and monomer emulsion feed. If polymerization is started with a part of the whole recipe r , polymerization will proceed only with r percent of the particles that would be formed with the same recipe using a batch process, provided that no new latex particles are generated during the ME feed. Gerrens² showed that for such a system, at a constant r , the narrowest PSD is obtained for the lowest monomer emulsion feed rate. It was men-

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tioned that the pre-period and the feed rate R_a determine whether or not new latex particles are formed during ME feed. There is a critical feeding time for such a system and, if that time is exceeded, no new particles are formed during the feed and the number of particles is independent of R_p . Similarly, there might be a critical pre-period time, above which secondary particle formation is completely suppressed.² If different distributions of ingredients between the initial charge and the feed are used, the particle formation rate is affected correspondingly. The effect of monomer distribution ratio on kinetic features of butyl acrylate semibatch emulsion polymerization was investigated earlier.³ Emulsifier distribution ratio $(R/F)_E$ is thought to be the most important variable in semibatch emulsion polymerisation using ME feed. If emulsifier is added in the course of polymerization in amounts below the critical micellar concentration (CMC), in order to avoid further micelle formation, the initial emulsifier loading will determine the number of particles to be formed during the polymerisation reaction.⁴ Crackeler and Naidus⁵ studied the effect of emulsifier distribution ratio and the feed rate on the kinetic features of semibatch emulsion polymerization of styrene. Their findings, however, have not received the specific attention that they deserved, perhaps due to the terminology that they have used to explain their results. They placed all the initiator in the initial charge and varied emulsifier distribution ratio. In this way, any difference between M-add and ME-add semibatch processes, in terms of initiator concentration, was avoided. By using two emulsifier distribution ratios, they showed that, as emulsifier concentration in the initial charge increases, the efficiency of added emulsifier in the formation of new particles is reduced and a PSD close to that of M-add is obtained. Snuparek⁶ claimed that for an acrylic emulsion butyl methacrylate/butyl acrylate/acrylic acid, except for low $(R/F)_E$ ratio and with various feeding time, particles with constant size were obtained. Subsequently, he reported similar results for emulsifier distribution in butyl acrylate/*N*-methacrylamide/acrylonitrile/ethylene glycol dimethylmethacrylate semibatch emulsion polymerization.⁷ There are some other reports in the literature regarding the various effects of distribution of a mixed emulsifier system on semibatch emulsion polymerization processes.^{8,9} Unzueta and Forcada,⁹ for example, showed that for unseeded semibatch emulsion polymerization of butyl acrylate/methyl methacrylate with mixed

emulsifiers, a narrower PSD with a larger average particle size was obtained when the ratio of anionic emulsifier to nonionic emulsifier was increased.

In on-line monitoring of particle formation in semibatch emulsion polymerizations with monomer emulsion feed, surface tension has been found of great importance because it is directly related to the concentration of free emulsifier in the aqueous phase. In interval *I* of a conventional batch emulsion polymerization, the newly nucleated growing particles adsorb additional emulsifier from the aqueous phase to become stabilized. However, the molecular emulsifier concentration in the water phase and also surface tension remain constant at the CMC as a result of the breakage of uninitiated micelles. When all micelles have disappeared, the emulsifier adsorption by growing particles from the aqueous phase is partly compensated by emulsifier release from shrinking monomer droplets. Consequently, there is a decrease in the concentration of free emulsifier, which results in a sharp increase in surface tension of the latex.¹⁰ The surface tension levels off in the beginning of interval III at a value well above that expected at the CMC, which is determined by the equilibrium distribution of emulsifier between oil and water phase.¹¹ Snuparek¹² was the first to report surface tension monitoring of semibatch emulsion polymerization reactors with monomer emulsion feed. He showed that three different kinds of surface tension variations may be encountered in a semibatch process with a monomer emulsion feed. If a high amount of emulsifier is present in the initial reactor charge, the same trend as that found in conventional batch polymerization is observed. In such a case, the amount of emulsifier added to the polymerization system is not enough to cover the surface of growing particles and most emulsifier molecules are swept from the aqueous phase by the growing particles. That leads to an increase in the surface tension. On the other hand, if no emulsifier is placed into the reactor before the addition of ME feed, a lower amount of particles will be formed in the course of polymerization and the amount of emulsifier continuously added to the reactor is sufficient to saturate the surface of particles. The surface tension decreases from that of water (or water saturated with monomer) to that found at the CMC and remains constant at this value. Between the two limiting cases, there is a third case in which the fraction of emulsifier in the initial reactor charge is very low and the

Table I Recipe Used for the Study of Monomer Initial Charge for Semibatch Emulsion Polymerization of BA

Runs ^a		Charge (g)					Feed (g)					
		BA	DDI	SLS	KPS	SBc	BA	DDI	SLS	KPS	SBc	
Set 1	SLS = 10.0 g/L											
	(R/F) _E											
1	0	0	100	0	0.054	0.054	250	400	5.0	0.216	0.216	
2	0.20	0	100	1.0	0.054	0.054	250	400	4.0	0.216	0.216	
3	0.50	0	100	2.5	0.054	0.054	250	400	2.5	0.216	0.216	
4	0.75	0	100	3.75	0.054	0.054	250	400	1.25	0.216	0.216	
Set 2	SLS = 2.50 g/L											
	(R/F) _E											
5	0	0	100	0	0.054	0.054	250	400	1.25	0.216	0.216	
6	0.20	0	100	0.25	0.054	0.054	250	400	1.0	0.216	0.216	
7	0.50	0	100	.625	0.054	0.054	250	400	0.625	0.216	0.216	
8	0.75	0	100	0.94	0.054	0.054	250	400	0.31	0.216	0.216	

^a Monomer feed rate = 185 g/h.

emulsifier concentration is around the CMC. With such a distribution the surface tension sharply increases at the beginning, due to rapid particle nucleation, and then decreases again to that of the CMC value. Unlike the first case, a smaller number of particles is formed in the other two cases, and particles are kept fully covered by a large amount of emulsifier fed into the reactor.¹² The importance of surface tension variation in semibatch emulsion polymerization, and its effect on particle formation and growth, has been reported in the literature.^{13,14}

In this research work, we investigate the effects of emulsifier distribution ratio on particle formation and particle size distribution in semibatch emulsion polymerization of butyl acrylate. The variations in surface tension with feeding time were also studied. Experiments were carried out using two overall emulsifier concentrations and four emulsifier distribution ratios. They are listed in Table I. No monomer was present in the initial reactor in these experiments.

EXPERIMENTAL

Chemicals

The butyl acrylate (BA), was supplied by Aldrich (99+%, inhibited with 10–15 ppm monomethyl-ether of hydroquinone) and was distilled under vacuum. The initiator, potassium persulfate (KPS), and the emulsifier, sodium lauryl sulfate

(SLS), were obtained from BDH and Fison Scientific, respectively, and were used as received. Sodium bicarbonate (SBc) was obtained from BDH and used as a buffer.

Apparatus and Latex Preparation

Polymerizations were carried out in a jacketed 1-L glass reactor equipped with a four-bladed flat turbine-type impeller, with a width of $\frac{1}{3}$ of vessel diameter, and standard four baffle plates.^{3,15} The stirrer rate was kept constant at 325 rpm. The temperature of the reactor contents was controlled at $50 \pm 0.50^\circ\text{C}$. The reactor was initially charged with the all components required for initial charge except the initiator. The initiator charge was dissolved in 20 cc of distilled deionized water (DDI) from the initial water charge. All of the ingredients were separately purged with nitrogen for 30 min and then transferred to the reactor. Then the reactor was heated to 50°C while being purged with overhead nitrogen for 30 min and then the initiator was added to the reactor. The start of the feeding to the reactor and the addition of initiator to the initial charge occurred simultaneously. The feed components were fed to the reactor using a dosing pump (MPI) and two different streams. Monomer was fed through the first stream and the aqueous solution of emulsifier, initiator and buffer was fed through the second stream. Both streams were initially purged with nitrogen for 30 min and then were kept in a blanket of nitrogen during feeding. The feeding

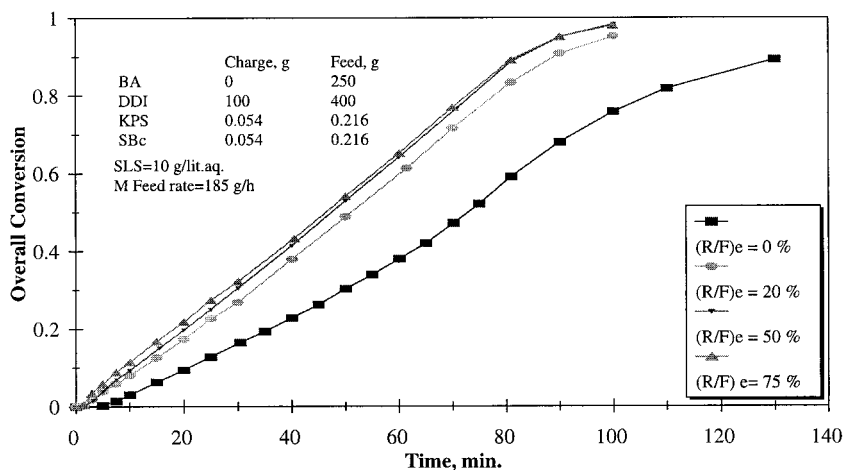


Figure 1 The time evolution of overall conversion for different emulsifier distribution ratios using SLS concentration of 10 g/L.

time of the two streams were set so that they both finished at the same time.

Analysis

Instantaneous conversion was measured using a gravimetry method. The overall conversion was calculated using a simple mass balance. Particle sizes were measured by photon correlation spectroscopy (PCS) and a transmission electron microscope (TEM). UV crosslinking was used for polymer hardening when TEM was used. 1000–1500 particles were counted to give a statistically satisfactory result, a larger number of particles was counted for the latexes with a wider size distribution. The number of particles N_p , was calculated using the expression

$$N_p = (6Mx_i / \pi\rho_p D_v^3) \quad (1)$$

where D_v is the volume average diameter of particles, M is the amount of monomer fed by the time t , and x_i is instantaneous conversion. The details are given elsewhere.¹⁵

Surface tension monitoring in semibatch experiments was achieved by taking samples of about 1–2 mL from the polymerization reactor at desired time intervals and placing them on watch glasses, covered by plastic lids to prohibit the gradual evaporation of the latex. Samples were kept small in order not to upset the behavior of semibatch processes. Samples were allowed to cool to room temperature. Generally 15–20 min was allowed for samples to reach thermodynamic equilibrium before any surface tension recorded.

Separate measurements showed that oxygen, from the surrounding air, inhibited any further reaction during that period. Surface tension measurements were made by using a Du Nouy ring tensiometer. Viscosity measurements were carried out for final latexes using a HAAKE viscometer.

RESULTS

The effect of emulsifier distribution between initial charge and the feed $(R/F)_E$ on the course of reaction has been studied at two overall emulsifier concentrations, 2.50 and 10.0 g/L. $(R/F)_E$ is the weight of emulsifier initially placed in the reactor divided by the whole emulsifier weight in the recipe. $(R/F)_E = 0$ means that no emulsifier was initially placed in the reactor, and $(R/F)_E = 1.0$ means that all the emulsifier was placed in the initial charge, which is identical to a batch operation. In these series of experiments, the initial emulsifier loading was kept at 0, 20 (or 25), 50, and 75 wt % of overall emulsifier concentration. The remaining emulsifier was fed to the reactor over 81.0 min at a constant flow rate of 185 g/h (based on the monomer). It should be noted that for all graphs and tables, the rate of addition given is based on the monomer feed.

The conversion-time curves are shown in Figures 1–3. A higher overall rate of polymerization was obtained for the higher overall SLS concentration, as was expected. For the lower SLS concentration, overall rate of polymerisation in-

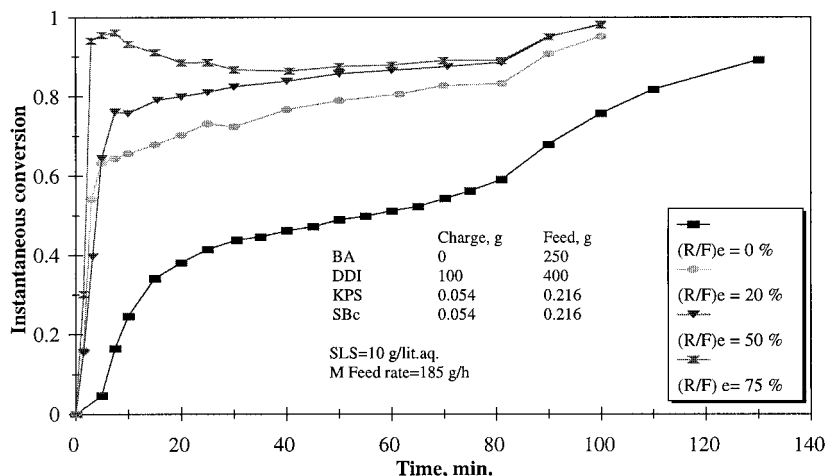


Figure 2 The time evolution of instantaneous conversion for different emulsifier distribution ratios using SLS concentration of 10 g/L.

creased with $(R/F)_E$, while it was virtually independent of $(R/F)_E$ for the higher SLS concentration. At a constant monomer emulsion feed rate, the steady state is reached earlier when a higher proportion of emulsifier is used in the initial charge, as is verified from Figure 1. The steady-state rate of reaction was only achieved for a few reactions. Inhibition periods, which increased with decreasing overall emulsifier concentration and $(R/F)_E$ ratio, were observed for almost all runs. A relatively long inhibition period was observed for the run using the lowest SLS concentration and $(R/F)_E$. During the inhibition period, monomer and emulsifier accumulated in the reactor so that when initiation started, a large

rate of polymerization was obtained. Therefore, the results obtained for this run were not taken into account for comparative study.

Figures 4 and 5 show the time evolution of polymer particles formed at various $(R/F)_E$ ratios for overall emulsifier concentrations of 10 and 2.5 g/L, respectively. For most runs carried out, an initial sharp increase in the number of particles was observed. The higher the $(R/F)_E$ ratio and SLS concentration, the longer the initial nucleation period. For SLS = 10 g/L, nucleation occurred at monomer-starved conditions for all $(R/F)_E$ ratios except for the $(R/F)_E = 0.0$. For experiments using 2.50 g/L of SLS, nucleation occurred at monomer-starved conditions only for

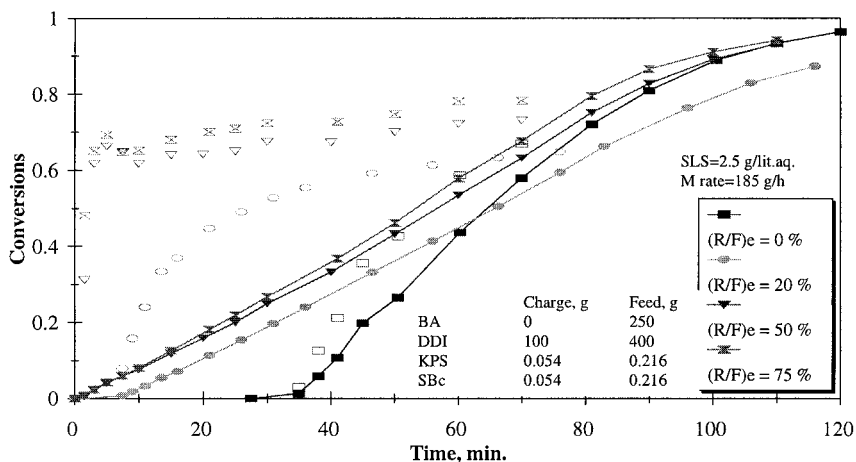


Figure 3 The time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different emulsifier ratios using overall emulsifier concentration of 2.50 g/L.

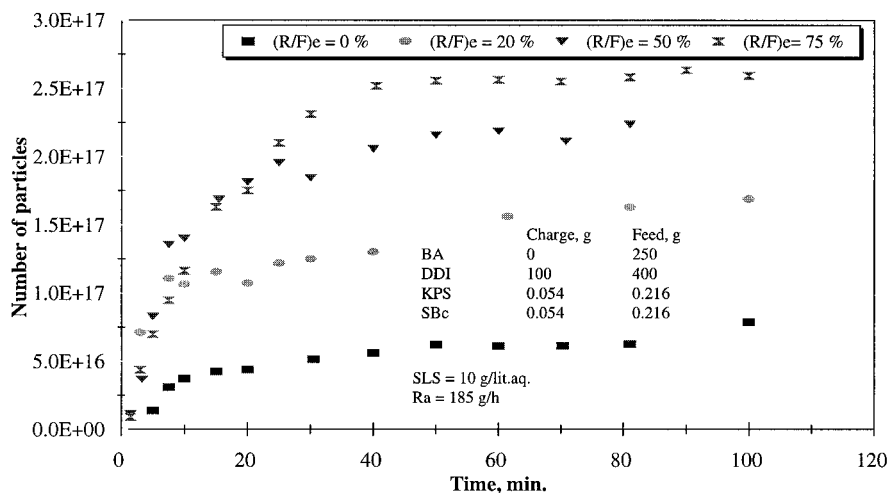


Figure 4 Number of polymer particles versus time for different emulsifier distribution ratios $(R/F)_E$ using SLS concentration of 10.0 g/L.

the two highest $(R/F)_E$ ratios (see Fig. 3). The occurrence of a long inhibition period for the run using SLS concentration of 2.50 g/L and $(R/F)_E = 0$, resulted in an accumulation of emulsifier in the reactor and the formation of a large number of polymer particles.

Figures 6 and 7 show the variation in surface tension with the progress of the reaction for the two series. A curve, different from the other curves, was obtained for SLS = 10 g/L when no emulsifier was initially placed in the reactor. Despite the different number of polymer particles formed at various emulsifier distribution ratios used, all surface tension-time curves followed almost the same trend except for $(R/F)_E = 0$, es-

pecially for the lower overall SLS concentration used. Figure 7 shows that the occurrence of a long inhibition period for $(R/F)_E = 0$ permits the reaction mixture to reach the CMC value before reaction can start. When reaction started, emulsifier micelles were depleted quickly and surface tension rose to a rather high value.

The PSDs have been grouped in Figures 8 and 9. The corresponding micrographs are presented in Figures 10 and 11. Table II details the average particle sizes and distributions of final latexes measured by TEM and PCS. Generally, the size data obtained by PCS was found mostly in satisfactory agreement with those obtained from TEM, if a correction is made.¹⁵ However, the discrep-

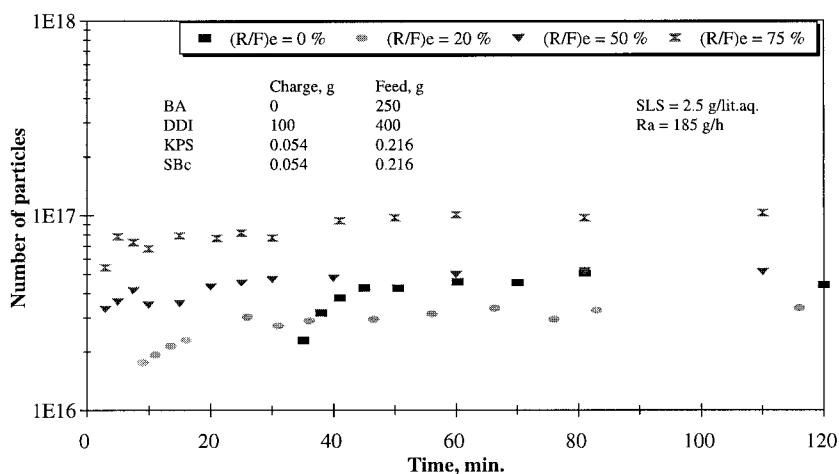


Figure 5 Number of particles vs time for different emulsifier distribution ratios $(R/F)_E$ using SLS concentration of 2.50 g/L.

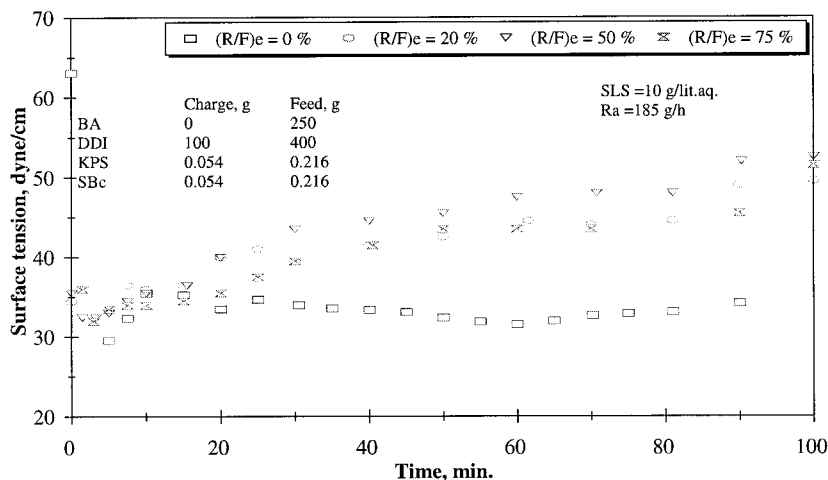


Figure 6 Evolution of surface tension with time for different emulsifier distribution ratios at SLS concentration of 10.0 g/L.

ancy increased with PDI of the latexes. The variation of PDI of final latexes with $(R/F)_E$ ratios shows a minimum at a medium $(R/F)_E$ ratio for both overall SLS concentrations. For SLS concentration of 10.0 g/L, a bimodal PSD was obtained for $(R/F)_E = 0$, while for higher $(R/F)_E$ ratios unimodal PSDs with broad distributions were obtained. For overall emulsifier concentration of 2.50 g/L, shorter nucleation periods were observed for all $(R/F)_E$ ratios studied, and as a result, sharper PSDs were obtained, compared with those from the same $(R/F)_E$ ratio but at the higher overall SLS concentration. Table II shows that for both overall SLS concentrations studied, the viscosity of final latexes increased with the

$(R/F)_E$ ratio, which correlates with the number of particles produced.

DISCUSSION

Rate of Polymerization

The steady state rate of polymerization was only established if the initial rate of polymerisation was rather high. This was achieved only for the higher overall SLS concentration (10 g/L) with high $(R/F)_E$ ratios. No steady state was obtained by using the lower SLS concentration. The variations in the rate of polymerisation over the rate of

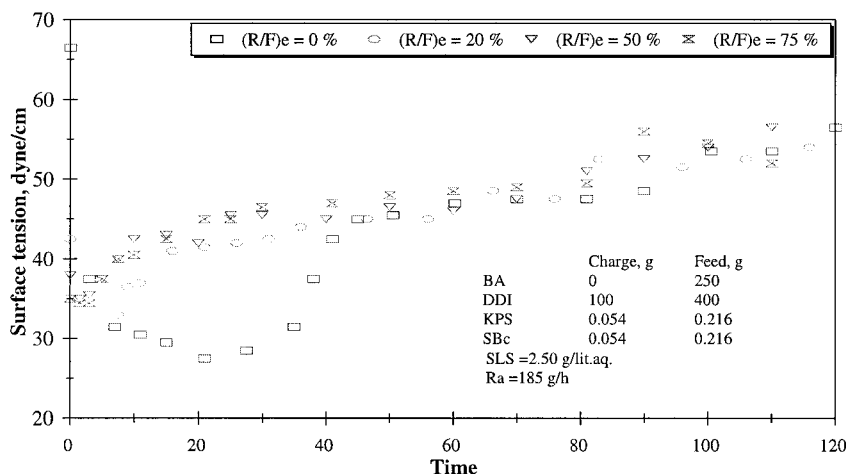


Figure 7 Evolution of surface tension with time for different emulsifier distribution ratios at SLS concentration of 2.50 g/L.

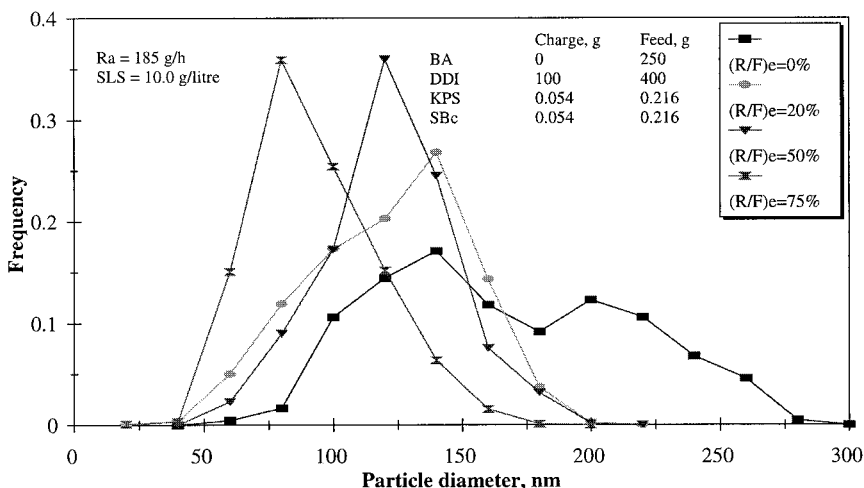


Figure 8 The PSD curves for latexes with different SLS distribution ratios using overall SLS concentration of 10.0 g/L.

monomer addition (R_p/R_a) vs $(R/F)_E$ ratio for the two overall SLS concentrations given in Table II indicate that the rate of polymerisation increases with $(R/F)_E$ ratio for the lower SLS concentration, while it stays practically constant and independent of $(R/F)_E$ for the higher SLS concentration.

Wesseling¹⁶ showed that the following equations apply to seeded systems with a constant number of polymer particles and constant radical concentration in the polymer particle phase, respectively:

$$\frac{R_p}{R_a} = \frac{K}{K + R_a} \quad (2)$$

$$\frac{R_p}{R_a} = 1.0 \quad (3)$$

where K is a constant given by

$$K = \frac{k_p N_p \bar{n}}{N_a V_m}$$

k_p is propagation rate constant, \bar{n} is the average radical number per particle, and V_m is the molar volume of monomer. No analytical expressions have been suggested so far for a semibatch process with monomer emulsion feed. The derivation of such a correlation can be quite complicated due

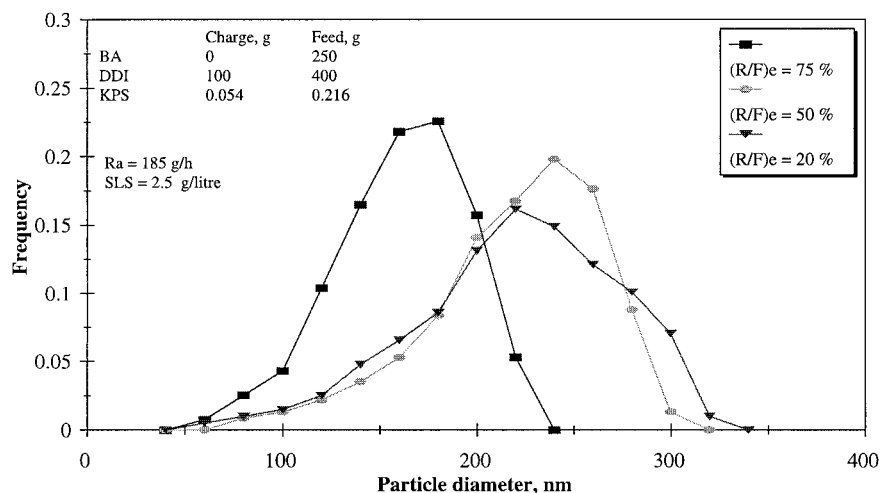


Figure 9 The PSD curves for latexes with different SLS distribution ratios using overall SLS concentration of 2.50 g/L.

to variation of emulsion properties in the course of reaction (number of particles and \bar{n}). ME-add semibatch polymerization processes differ from M-add semibatch process in two important ways. First, particle nucleation may continuously occur in the course of reaction through secondary nucleation due to continuous addition of emulsifier. Second, the average radical number in polymer

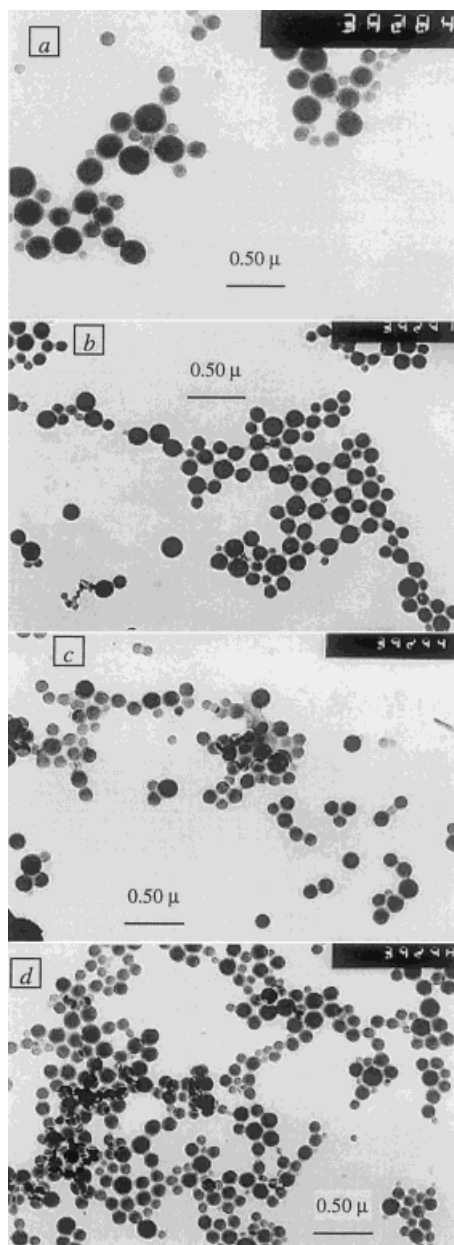


Figure 10 Micrographs for the final latexes using different emulsifier distribution ratios at SLS concentration of 10 g/L (runs BK, BM, BN, BO) corresponding to Figure 8. (a) $(R/F)_E = 0\%$, (b) $(R/F)_E = 20\%$, (c) $(R/F)_E = 50\%$, and (d) $(R/F)_E = 75\%$.

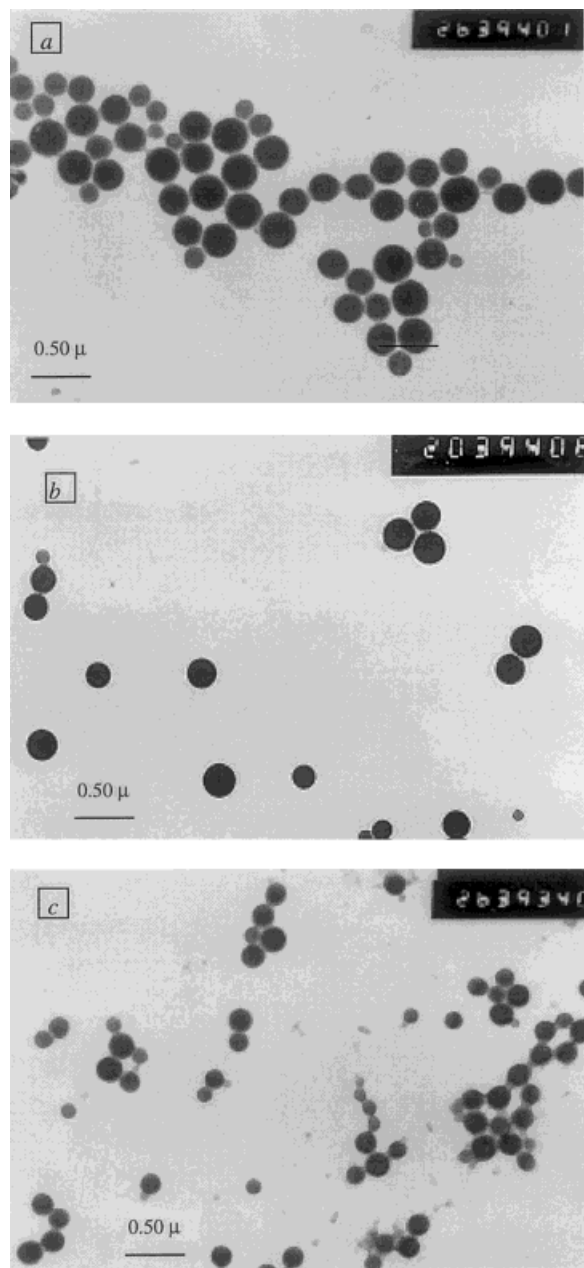


Figure 11 Micrographs from the final latexes using different emulsifier distribution ratios at SLS concentration of 2.50 g/L (runs BR, BP, BQ), corresponding to Figure 9. (a) $(R/F)_E = 20\%$, (b) $(R/F)_E = 50\%$, and (c) $(R/F)_E = 75\%$.

particles may increase due to addition of initiator. The first factor might not be very important for Case III and Case I kinetics where the rate of polymerization is only slightly influenced by the number of polymer particles. For BA emulsion polymerization, it has been reported that Case I kinetics is more pertinent than Case III, which

once was considered to be applicable.^{17,18} The addition of initiator can increase the radical number in the polymer particles for both Case I and Case III kinetics. Both or either of these two factors can increase the total number of radicals ($N_p \bar{n}$) with time and enhance the rate of polymerization. In such a case K is not constant in the course of reaction and eq. (2) obviously does not apply.

All previous studies regarding the application of these equations have used different feed rates. Here, we attempt to evaluate such an applicability for different K values at a constant feed rate ($R_a = \text{constant}$), which is the case for the current series of experiments. K could be varied by changing the number of particles and radical number. If the variation in K in the course of reaction is confined to a constant radical concentration in the polymer particles ($N_p \bar{n}/V_p = \text{constant}$), then it can be expected that eq. (3) holds for the system. Table II shows that the ratio of steady-state rate of polymerisation over rate of monomer addition is less than one, $R_p/R_a < 1.0$, indicating that eq. (3) does not apply to the current study.

For eq. (2) to hold, K values could be varied for different SLS concentrations and distributions, but have to be practically constant during the steady-state period. Application of eq. (2) requires that instantaneous conversion does not change with time during feeding for any constant K value; $x_{ss} = R_p/R_a$.¹⁵ For an M-add semibatch emulsion polymerization of BA using a constant N_p (and constant amounts of SLS and KPS in the reactor charge), it was reported¹⁵ that steady-state rate of polymerization is confined to the eq. (2). Figure 2 shows that for the ME-add semibatch process studied here, the instantaneous conversion is not constant and increases with time, at least for the two $(R/F)_E$ ratios of 20 and 50%, despite the overall steady-state rate of reaction (R_p) for the three highest $(R/F)_E$ being practically constant, as shown in Figure 1. This implies that in these series of experiments ($N_p \bar{n}$) and hence K were not constant in the course of feeding, indicating that eq. (2) does not apply to the current ME add system either.

For M-add semibatch emulsion polymerization of BA at a constant monomer feed rate, a larger steady-state rate of polymerization, and thus a larger x_{ss} , was obtained for the higher SLS concentration in the charge. However, x_{ss} stayed practically constant during steady state, which allows eq. (2) to hold. The increase in the overall steady-state rate of polymerization with SLS concentration for BA, which shows a Case I kinetic

behavior, was attributed to the acceleration in the rate of initiator decomposition in the presence of SLS and BA.^{3,15} Thus, for an ME-add semibatch process using different emulsifier distribution ratios, the SLS balance in the reactor, or in the aqueous phase, is the third factor that can contribute to the variation in K with time.

Number of Particles

Particle nucleation in semibatch emulsion polymerization reactors with monomer emulsion feed is highly dependent on the distribution of the emulsifier between the charge and the feed. If no emulsifier is initially present in the reactor, the emulsifier concentration in the feed and the feed rate will determine the number of polymer particles. As the emulsifier concentration in the initial charge increases, the behavior of an ME-add semibatch process becomes more similar to an M-add semibatch process or conventional batch process where a single nucleation stage is usually observed during the reaction. According to Smith–Ewart theory, a larger number of particles is expected if a larger amount of emulsifier in the reactor charge [larger $(R/F)_E$] is used. Snuparek⁶ investigated particle formation for semibatch emulsion polymerization of acrylic monomers. He reported that above an emulsifier distribution ratio of 15%, a constant number of particles was obtained for varying $(R/F)_E$ values. This indicated that a large number of primary particles underwent extensive limited flocculation. This claim, that the number of particles is determined by the emulsifier concentration in the whole recipe and is independent of the way it is added to the reactor, has also been reported by Uroquila et al.¹⁹ for homogenous nucleation in the seeded semibatch emulsion copolymerization of vinyl acetate and methyl methacrylate. Vanderhoff²⁰ summarized reported works on the effect of emulsifier concentration in batch emulsion polymerization reactors and suggested that a plot of number of particles vs emulsifier concentration should be an S-shaped curve. The near horizontal curve at emulsifier concentrations well above the CMC was suggested to be due to a controlling effect of radical generation in the aqueous phase. An S-shaped plot of N_p vs emulsifier concentration has been reported by other investigators.²¹ Song and Poehlein²² simulated the variation of particle number at the steady state and transient state with micelle concentration and obtained the S-shaped curve for all monomer types. It is expected

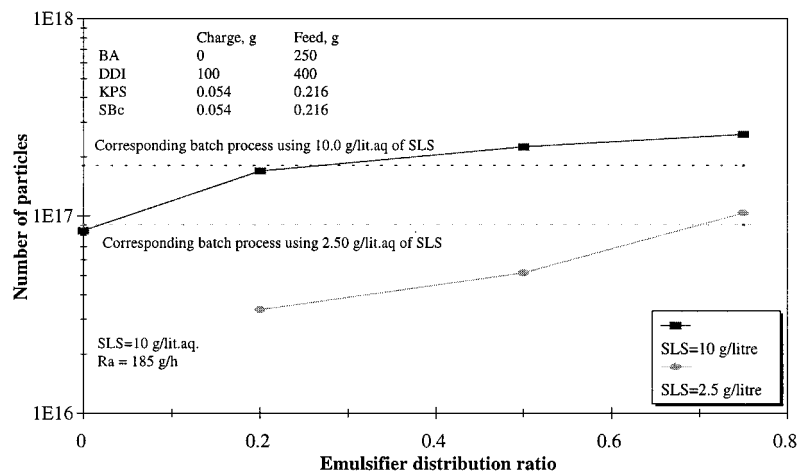


Figure 12 Variation of number of polymer particles with emulsifier distribution ratio $(R/F)_E$, for two overall emulsifier concentrations, 2.50 and 10.0 g/L.

that the higher limit of N_p for a semibatch process is reached at a much lower emulsifier concentration, compared to a batch process, due to enhanced particle formation at monomer starved conditions. Figure 12 shows the variation in the number of polymer particles vs emulsifier distribution ratio at two overall emulsifier concentrations, 10 and 2.5 g/L, respectively. The two curves demonstrate a different trend in variation of N_p vs $(R/F)_E$. It is seen from the figure that, at the high emulsifier concentration, the number of polymer particles initially increases with $(R/F)_E$ ratio, and then at higher $(R/F)_E$ values (above 20%) it remains almost constant and shows a little increase with $(R/F)_E$ afterward. While at the lower overall SLS concentration N_p increases almost linearly with $(R/F)_E$ ratio, implying that the emulsifier concentration in the reactor charge is controlling the number of polymer particles. Thus, it can be concluded that the final number of particles may be controlled by overall emulsifier concentration and be independent of the way it is added to the reactor only for high SLS concentrations and specially for the higher range of $(R/F)_E$ ratios. For a low emulsifier concentration, emulsifier distribution ratio plays an important role in determining the final number of particles. It should be noted that as monomer emulsion feed rate is increased, more emulsifier molecules can contribute to the nucleation and the effect of variation of $(R/F)_E$ on the number of particles decreases.

Some other indications can be obtained by cross-examination of the runs having constant SLS concentration in the charge and different

SLS concentration in the feed, and vice versa. Figure 13 reveals that when the polymerization reaction starts with 2.0 g/L of SLS in the initial charge, the variation in amount of SLS in the feed from 0.75 to 8.0 g/L can only slightly increase the number of polymer particles. But when polymerization starts using either 0 or 7.50 g/L, SLS in the initial charge and 2.50 g/L SLS in the feed, a large difference in the number of particles is obtained. The extent of this difference can be even larger than that shown in Figure 13, because N_p for the run using no SLS in the charge (run 5) is enhanced by accumulation of emulsifier in the system due to long inhibition period, as discussed before. This comparison indicates that the emulsifier concentration in the charge is mostly used for particle formation, while the emulsifier in the feed has less contribution to the particle formation and is mostly used for particle stabilisation.

Another important conclusion can be drawn from Figure 12. The two horizontal lines on this graph show the number of final particles for the equivalent batch processes using overall SLS concentration of 2.50 and 10.0 g/L. This graph clearly shows that an ME-add semibatch emulsion polymerization process can produce more particles than a conventional batch process if suitable conditions exist, i.e., monomer-starved conditions. Traditionally, batch and semibatch emulsion polymerization processes are rated for particle generation as M-add semibatch, batch, and ME-add semibatch process.^{2,4,5} It was shown before that the M add semibatch process is always superior to a batch process, in term of number of particles.³ For ME-add semibatch process, according to Fig-

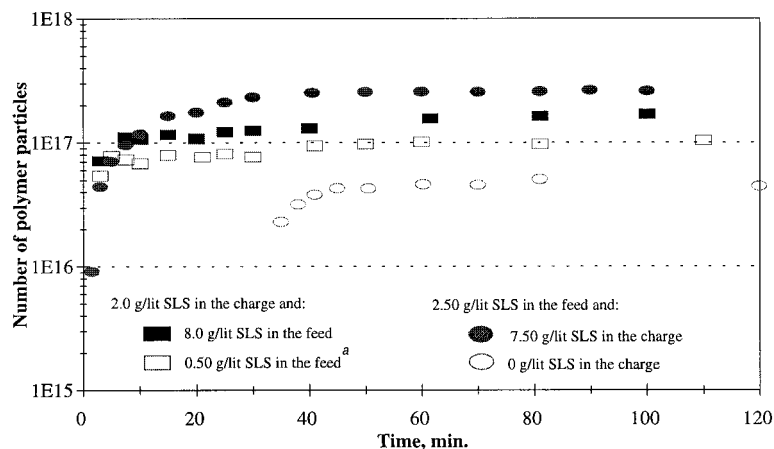


Figure 13 Variation of number of polymer particles with time for different emulsifier distribution between the charge and the feed (a: the figures are rounded).

ure 12 for low $(R/F)_E$ ratios, a batch process is superior to the ME add semibatch process in terms of number of particles. However, above a critical $(R/F)_E$ ratio for any fixed recipe and polymerization conditions, the ME-add semibatch process can produce more particles than a batch process. The critical $(R/F)_E$ ratio decreases with overall SLS concentration, as can be inferred from Figure 12. By taking into consideration that only 20 wt % of overall initiator concentration was initially placed in the reactor charge for the semibatch run, and the rest was fed to the reactor along with monomer emulsion feed, we can conclude that ME-add semibatch process can perform better than a batch process in terms of number of particles formed. The capability of an ME-add semibatch process to produce more particles than the equivalent batch process increases with increasing SLS concentration and decreasing feed rate.

Snuparek⁶ showed that for an acrylic emulsion polymerization with $(R/F)_E = 0$, surface tension decreased from a value over 60 dyne/cm to a value close to 30 dyne/cm, and stayed there afterward. The experiment for $(R/F)_E = 0$ using SLS concentration of 10.0 g/L resulted in the same type of surface tension variation with time; an initial decrease from values around 60 dyne/cm to values close to 30 dyne/cm, but with a minor difference from what was reported by Snuparek because surface tension increased to values around 35–37 dyne/cm and eventually over some period of time ended with a practically constant, but substantially low surface tension, as shown in Figure 6. It should be noted that at monomer-starved condi-

tions if the reaction mixtures reaches the CMC value then it remains at the CMC till the end of reaction. This is obviously because the emulsifier needed to cover the surface of particles varies roughly with the $\frac{2}{3}$ power of monomer feed rate.¹³ At such a condition, particle nucleation might continue to the end of feeding.

As more particles are formed with increasing $(R/F)_E$, more particle surface area is developed and less emulsifier is available in the feed to cover the particles, resulting in a diminishing particle surface coverage with feeding time. This is in accord with $\frac{2}{3}$ power dependence of particle surface area on monomer feed rate which results in an increasing surface tension with time. Early in the reactions surface tension rose to around 35.0–40.0 dyne/cm quickly and then increased above that in shorter increments, depending on the overall emulsifier concentration and distribution. However, the differences between surface tension variation with time for different overall emulsifier concentrations and emulsifier distribution ratios were not appreciable. The increase in surface tensions during feed addition observed from Figures 6 and 7 are different from the constant steady-state surface tensions reported by Snuparek⁶ [except those for $(R/F)_E = 0$]. One possible reason for such a steady state could be particle coagulation in the course of feed addition. As particles grow, they might become less covered by emulsifier molecules, lose their stability, and coagulate. The coagulation events would result in a reduction of total surface area of particles, and thus tend to maintain the balance between emulsifier molecules dissolved in the aqueous phase

and those adsorbed on the surface of particles, leading to a constant steady-state surface tension. An appreciable particle flocculation was reported by Snuparek. Another possible reason for steady-state surface tension could be the contribution of *in situ* surfactants and anchored groups generated by persulphate initiator to the balance of surface active agents in the system and the development of surface tension. By developing a model that takes into account the effects of added surfactants, *in situ* surfactants, and anchored sulphate groups, Wang et al.¹⁴ showed that a flat surface tension variation profile can be explained by the contribution of *in situ* surfactants and anchored groups. Obviously, such an effect is enhanced at a higher temperature where the rate of initiator decomposition is very high, which again is consistent with the experimental conditions (80°C) used by Snuparek.^{6,7} It should be noted that surface tension of the emulsions is reduced in the presence of monomers dissolved in the aqueous phase. The monomer concentration in polymer particles decreases with time in the course of feeding, as can be inferred from Figures 2 and 3. Since monomer concentrations in the polymer particles and in the aqueous phase are in thermodynamic equilibrium, it can be assumed that surface tension variation can be partly due to variation of instantaneous monomer conversion in the course of reaction.

Particle Size Distribution

For BA batch emulsion polymerization, using similar conditions to those used here, a monomodal PSD was reported.¹⁸ Thus, the evolution of a bimodal PSD for the current system requires that particle formation occurs at two or more intermittent time intervals, or that particle formation is interrupted by a period with a low nucleation rate. For all distribution ratios, the particles were initially formed through monomer-flooded, and then monomer-starved, nucleation [except for $(R/F)_E = 0.0\%$] while the fresh emulsifier was added to the reactor and that contributed to the particle nucleation. A bimodal PSD was obtained if no emulsifier was present in the initial charge, in accord with the findings of Snuparek.⁶ This is the condition that satisfies a low rate of particle formation in the initial stage of the reaction. The rate of secondary nucleation was enhanced, since the concentration of initial particles was not enough to adsorb incoming emulsifier molecules onto their surfaces so that emulsifier concentra-

tion in the aqueous phase builds up. A bimodal PSD with the PDI equal to 1.25 was obtained for $(R/F)_E = 0$. As $(R/F)_E$ increases, the number of particles formed during the initial stage of reaction increases, and hence the contribution of secondary nucleation is hindered, resulting in an emerging of a unimodal PSD. This is associated with a narrowing of PSD and a smaller value for PDI. As $(R/F)_E$ is further increased, the possibility of secondary nucleation is totally removed by a large number of polymer particles formed that can adsorb incoming emulsifier molecules, and a broad PSD is obtained. The occurrence of a broad PSD is a result of the presence of a high SLS concentration in the charge, which allows particle formation to proceed mostly at monomer-starved conditions. Particles nucleated at different times have correspondingly different lengths of time to grow until the end of feeding. This gives rise to polydispersity of polymer particles with increasing $(R/F)_E$. The duration of primary nucleation and the occurrence of secondary nucleation and their variations with $(R/F)_E$ can be observed in Figure 4. More explanations about monomer-starved nucleation can be found elsewhere.^{3,5,15}

Figure 14 shows that for SLS concentration of 10 g/L, particle surface excess ratio stays at saturation level in the initial stage of reaction. The details for estimation of particle surface excess ratio was given elsewhere.³ The surface excess ratio equal to or greater than one means that particles are fully covered by emulsifier molecules. The surface excess ratio smaller than one is equivalent to particle surface coverage ratio and means that particles are not fully covered by emulsifier molecules. The interval of primary particle formation through micellar nucleation can be inferred from Figures 4 and 14, which show that particles are nucleated in a longer period of time for higher $(R/F)_E$, as it is expected. For $(R/F)_E = 0$, particle surface excess ratio approaches one, but for the other $(R/F)_E$ ratios used, the coverage ratio shows a very mild decrease with time. It can be concluded that for $(R/F)_E = 0$, secondary nucleation occurred through homogeneous nucleation, since no emulsifier micelles were present in the reaction mixture.

For the lower SLS concentration, 2.50 g/L, PDIs show the same trend with $(R/F)_E$ ratio as those for the higher SLS concentration, but with lower variations (see Table II). This is because, for this case, primary particle nucleation occurred briefly in the beginning of reaction at monomer flooded conditions, as can be inferred from Figure

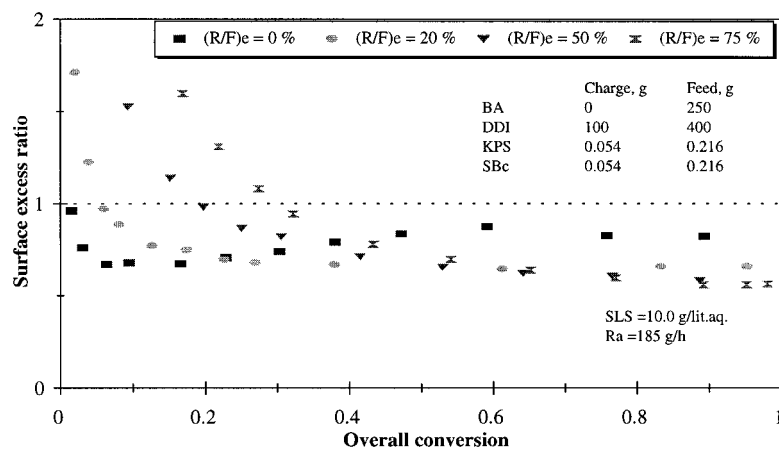


Figure 14 Particle surface excess ratio vs overall conversion for different emulsifier distribution ratios at SLS concentration of 10.0 g/L.

15. Secondary nucleation did not occur for these runs because the emulsifier concentration in the feed was not sufficient to increase the surface coverage of particles to a level where particle nucleation and stabilisation were possible. The corresponding variations in surface excess ratio with conversion for batch experiments using overall SLS concentration of 10.0 and 2.5 g/L are shown in Figure 16. For the batch experiments the surface coverage ratios dropped to constant values in the beginning of interval III (conversion of 0.40–

0.45). From the comparison of Figures 14–16 it can be seen why the addition of a surfactant into a semibatch reactor can enhance the particle stability and hence increase the possibility of secondary nucleation.

Generally, as the $(R/F)_E$ ratio increases, particle formation in an ME-add semibatch process follows the same trend as that in the M-add semibatch process. The results obtained indicate that the time evolution of the number of polymer particles for semibatch emulsion polymerization with

Table II Number (D_n), Weight (D_w), Volume (D_v), Intensity (D_I) Average Diameters and PDI Obtained by Calibrated TEM and Average Diameter (D_z) Obtained by PCS of Final Latexes for Different Emulsifier Distribution Ratios, and (R_p/R_a) During Steady State

Run	$(R/F)_E$ (%)	(R_p/R_a) (%)	X_f^d (%)	Viscosity MPa · s	PCS (nm) D_z	TEM (nm)				
						D_n	D_w	D_v	D_I^b	PDI
SLS = 10 g/L										
1	0	—	89	44.1	213	156	196	170	209	1.25
2	20	90	95	59.0	153	112	131	119	137	1.17
3	50	92	89	69.4	136	112	127	117	133	1.13
4	75	91	98	82.2	134	83	103	90	112	1.23
SLS = 2.50 g/L										
5 ^a	0	—	95	—	223	207	217	212	220	1.05
6	20	75 ^c	93	35.6	256	211	240	222	248	1.14
7	50	83 ^c	94	43.5	226	212	233	220	239	1.10
8	75	87 ^c	87	43.6	180	151	169	158	174	1.12

^a Note that for this run polymerization occurred with a long inhibition period and the results can not be used for a comparative study.

^b D_I is equivalent to D_z measured by PCS.

^c For these runs steady-state rate of polymerisation were not achieved. Here R_p stands for the average rate of polymerization in the second half of feeding time. R_a is the rate of monomer addition.

^d Final monomer conversion.

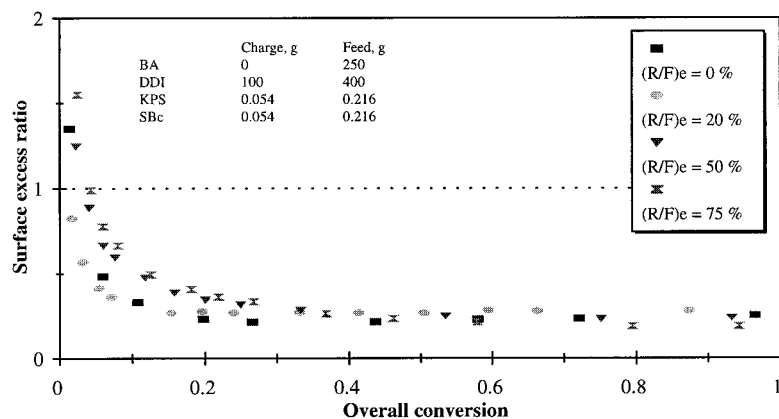


Figure 15 Particle surface excess ratio vs time for different emulsifier distribution ratios at SLS concentration of 2.50 g/L.

ME feed can be characterized by a relatively long nucleation period and a bimodal or skewed PSD for high overall emulsifier concentration, and a short nucleation period and a comparatively sharper PSD for low overall emulsifier concentration in the reactor charge. For both emulsifier concentrations, PDI initially decreased with increasing $(R/F)_E$ ratio and then, after reaching a minimum, increased with $(R/F)_E$ ratio.

CONCLUSION

It was found that the traditional ranking of polymerization processes in terms of number of particles produced is not always justified. The number of particles in semibatch emulsion polymerisation is mainly determined by two opposing

factors: (1) monomer-starved nucleation, and (2) partitioning of ingredients between the initial charge and the feed. Particle formation at monomer-starved conditions would result in a larger number of particles, due to suppressed growth rate of particles. The partitioning factor might have opposing effects on the particle formation. For a fixed recipe, as more emulsifier and initiator are placed in the initial charge, the semibatch process approaches a batch process and more particles are formed, while the addition of monomer to the initial charge will favor monomer-flooded nucleation and reduces the number of particles. The net effect between monomer-starved nucleation and emulsifier partitioning will decide the number of particles. The number of particles obtained from an ME-add semibatch process is usually lower than that from a batch process due to

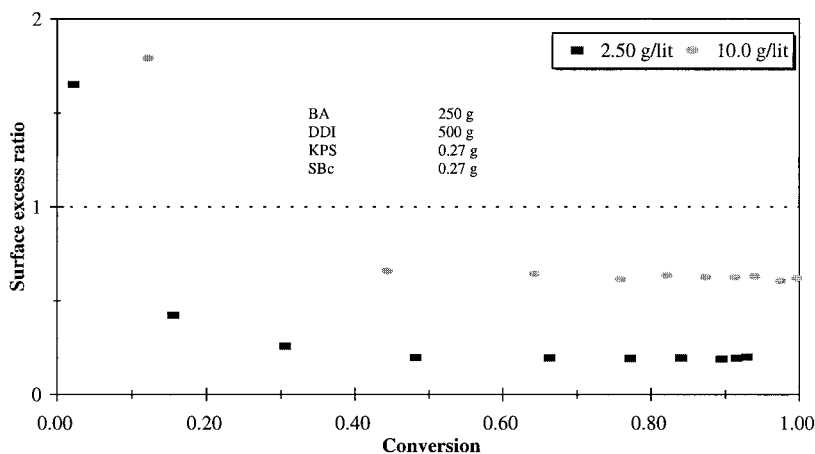


Figure 16 Particle surface excess ratio vs time for BA batch emulsion polymerisations using different SLS concentrations of 2.50 and 10.0 g/L.

partitioning of emulsifier, or initiator, between the precharge and the feed. However, it is possible to enhance particle formation through monomer-starved conditions by using a low monomer emulsion feed rate so that a larger number of particles is obtained for ME-add compared to batch and even M-add semibatch processes. The ranking of emulsion polymerization processes can be best performed in terms of the maximum number of particles which can be produced. An M-add semibatch process always provides the largest number of particles among the other processes studied. The ranking of batch and ME-add semibatch processes in terms of number of particles depends on the polymerisation conditions. A larger number of particles can be obtained from an ME-add semibatch process, compared to that from a batch process, if particle formation occurs at monomer-starved conditions.

Initially, the PDI of the final latexes decreased with increasing $(R/F)_E$, until a minimum was reached and then the PDI increased again. Using emulsifier in the initial charge will reduce the possibility of formation of bimodal PSD curves by increasing the rate of primary nucleation. However, application of an initial amount of monomer charge to a semibatch emulsion process with monomer emulsion feed has the opposite effect by reducing the extent of primary nucleation and hence increasing the possibility of secondary nucleation.³

A rather constant steady-state surface tension was obtained only if no emulsifier was placed in the initial reactor charge and a sufficient amount of emulsifier was present in the feed. For other emulsifier distribution ratios used, no steady-state surface tension was obtained.

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