

Semibatch Emulsion Polymerization Of Butyl Acrylate. I. Effect of Monomer Distribution

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ABSTRACT: The effects of initial monomer charge on the particle formation and on the rate of polymerization were investigated for semibatch emulsion polymerization of butyl acrylate using sodium lauryl sulfate (SLS) as a surfactant and potassium persulfate (KPS) as an initiator. For the semibatch process with monomer (M) feed, it was found that by varying the monomer distribution ratio between the initial reactor charge and the feed it is possible to alter the contribution of monomer-flooded and monomer-starved nucleation mechanisms to the whole nucleation process. The number of particles increases as the initial monomer charge decreases, if the monomer concentration is below a critical value for any fixed system. The increase in number of particles is associated with a broad particle-size distribution which might depict an emerging second peak on the particle-size distribution curve. For low emulsifier concentration systems, a larger number of particles was obtained for a lower amount of monomer charge. Particle coagulation and emulsifier adsorption on the monomer droplets were counted as the main reasons for such behavior. For a semibatch process with monomer emulsion (ME) feed, the larger number of particles was formed at a lower initial monomer charge, similar to an M -add semibatch process. However, the application of monomer charge to an ME -add process was found to increase the possibility of secondary nucleation and led to the occurrence of a bimodal particle-size distribution. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3094–3110, 1999

INTRODUCTION

In recent years, many publications have appeared in the literature regarding semibatch emulsion polymerization. Semibatch emulsion polymerization is a versatile process by which many of high-value added polymer latexes with special particle morphology and composition can be produced. Naidus and Krackler,^{1,2} Gerrens,³ and Wesseling⁴ pioneered the more systematic research on the kinetic features of semibatch emulsion polymerization processes. They have compared batch, semibatch with monomer feed (M -add semibatch), and semibatch with monomer emulsion

feed (ME -add semibatch) and concluded some general guidelines.

Since semibatch emulsion polymerization is usually started with a seeding batch stage, it is important to investigate parameters which can affect the kinetics of the seeding batch operation. The seeding batch is the most critical stage of a semibatch process, because it controls particle formation in the whole course of the reaction. For a semibatch process with M feed, the most important parameter is the monomer initial charge, since this mode of operation starts with all the reaction ingredients, except part of the monomer, in the reactor. The monomer initial charge can vary from a small to a big proportion of the whole monomer in the recipe. For a semibatch process with ME , not only the monomer distribution ratio but also the distributions of other components,

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especially an emulsifier, have a great effect on the particle formation.

Following the Harkins⁵ original description of the mechanism of emulsion polymerization, and according to the quantitative theory developed by Smith and Ewart,⁶ emulsion polymerization behavior (in batch reactors) can be divided into three intervals: In interval I, which is usually referred to as the "nucleation or particle-formation stage," free radicals generated in the aqueous phase enter micelles and form new polymer particles. The end of interval I is marked by depletion of all uninitiated micelles and a cessation in the particle-formation cycle. In interval II, particles grow as they are continuously fed with a monomer by monomer droplets. This interval is usually referred to as the "particle-growth stage." The end of interval II is marked with depletion of all monomer droplets. In interval III, polymerization continues in the monomer that remains within the particles. During interval III of a batch process, monomer concentration in the polymer particles is not maintained at saturation conditions and decreases with time. When monomer droplets are no longer present, latex particles are unable to swell to their saturation equilibrium size and the aqueous phase will not be saturated with the monomer.

Two types of semibatch operations have been defined in the literature: monomer-flooded and monomer-starved. In the first type, the rate of monomer addition is higher than the maximum polymerization rate attainable by the system. The monomer accumulates in the system as monomer droplets and the polymer particles are saturated with the monomer, as in interval II of a batch operation. In the second type, the rate of addition is lower than the rate of polymerization and the polymerization reaction occurs in interval III where particles are not swollen to their maximum size. Correspondingly, the terms monomer-flooded and monomer-starved nucleations can be used to identify the two different nucleation patterns in these two regions.

For conventional batch emulsion polymerization, it is generally accepted that the particle number is not influenced by the monomer concentration, or monomer/water ratio, and only the final particle size is determined by the monomer/water (M/W) ratio. Chatterjee et al.⁷ and Nomura and Harada⁸ found that a larger number of latex particles is formed at very low M/W ratio than that at high M/W ratio using a constant emulsifier concentration. Dunn⁹ ex-

plained that, when the amount of monomer is reduced below the amount required to saturate the emulsifier micelles with a solubilized monomer, it is likely that the rate of polymerization in the latex particles will ultimately become diffusion-controlled, reducing the rate of dilatation so that the surface of growing particles can be kept continually saturated with the adsorbed emulsifier precluding all particle coalescence. Dunn's hypothesis is based on the assumption that in the conventional emulsion polymerization (high M/W) the rate at which the emulsifier is adsorbed on the polymer particles in the presence of emulsifier micelles may be insufficient to saturate the surface layer of the latex particles. This explanation has been rejected on the ground of a high rate of mass transfer for anionic emulsifiers.¹⁰

The initial monomer loading in a semibatch process might have a major effect on particle formation and growth. Naidus¹ stated that the elimination of monomer droplets from the initial charge increases the emulsifier/monomer ratio (M/E) and makes more emulsifier molecules available to contribute to particle formation. It was shown by Krackler and Naidus² that a larger number of particles can be formed in a semibatch operation due to a reduced growth rate of particles. No significant difference in the average particle size and distribution was observed with an increasing feed rate for styrene, methyl acrylate, and vinyl acetate monomers with a fixed monomer initial charge.^{2,3,11} According to Gerrens,³ latexes made by an M -add semibatch process show the same particle-size distribution as those made by the batch process. However, such a conclusion should not be generalized and must be verified for different polymerization conditions.

To the knowledge of the present authors, while the effects of the monomer initial charge might be considered theoretically, no experimental data have been reported regarding them. The objective of this article was to investigate the effect of the monomer distribution ratio between the initial reactor charge and the feed, $(R/F)_M$, in the semibatch emulsion polymerization of butyl acrylate (BA) using both M -add and ME -add modes. A comparative study of batch and semibatch operations is also presented. For all experiments, the overall M/W ratio was kept constant at 1/2. Overall initiator and buffer concentrations were both 0.54 g/L.

EXPERIMENTAL

Chemicals

BA was supplied by Aldrich (Gillingham, UK) (99+%, inhibited with 10–15 PPM MEHQ) and was distilled under a vacuum at 52.5°C. The initiator, potassium persulfate (KPS), and the emulsifier, sodium lauryl sulfate (SLS), were obtained from BDH (Poole, UK) and Fison Scientific (Loughborough, UK), respectively, and were used as received. Sodium bicarbonate (SBc) was obtained from BDH and used as a buffer.

Apparatus

Polymerizations were run in a jacketed 1-L glass reactor equipped with a four-bladed flat turbine-type impeller with a width of $\frac{1}{3}$ of the vessel diameter, standard four-baffle plates with the width of $\frac{1}{10}$ of the vessel diameter located at 90° intervals, an overhead reflux condenser, a thermocouple, a sampling device, sampling port for nitrogen purge, and an inlet for feeding ingredients. The stirrer rate was kept constant at 325 rpm. The position of the stirrer blades was adjusted, during polymerization, to be 2–3 cm from surface to avoid the formation of a free monomer layer. The temperature of the reactor contents was controlled by pumping water with an appropriate temperature through the jacket. Since all polymerization started with a small part of the monomer in the reactor, the heat of reaction was low and a better temperature control over the reactor was obtained, compared with the batch operation. The temperature of the reactor contents was controlled at $50 \pm 0.50^\circ\text{C}$. Sampling was carried out at the desired time interval by removing an aliquot of 1–2 g latex with a hypodermic syringe.

Latex Preparation

The reactor was initially charged with all the components required for the initial charge except for the initiator. The initiator charge was dissolved in 20 cc of distilled deionized water (DDI) from the initial water charge. All 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 rate of nitrogen bubbling was decreased in order to minimize evaporation. In the semibatch experiments with *M* feed only, part of the monomer together with all of the emulsifier, initiator, buffer, and

water were placed in the initial charge and the rest was fed into the reactor using a reciprocating pump (MPL) at a constant rate. In the semibatch experiments with the monomer emulsion feed, only part of the monomer together with parts of emulsifier, initiator, buffer, and water were placed in the initial charge and the rest was fed to the reactor using two different streams. The monomer was fed through the first stream and the aqueous solution of the emulsifier, initiator, and buffer was fed through the second stream. Both streams were initially purged with nitrogen for 30 min and then kept in a blanket of nitrogen during feeding. The feeding time of the two streams, for the *ME*-add operation, were set so that they finished at the same time. For all runs, inhibition periods in the order of 0.5–5.0 min were observed. The time zero for the start of the reaction was taken when an infinitesimal increase in the reactor temperature was detected by a very sensitive thermocouple. Monomer addition was started after a preperiod of 2.50 min for the *M*-add operation. No preperiod was considered for the *ME*-add operation. It should be noted that for all graphs and tables the rate of addition given is based on the *M* feed.

Analysis

Conversion

Aliquots of about 1–2 g were withdrawn with a syringe at appropriate intervals and poured into a small weighed aluminum foil dish. Methanol containing a small amount of hydroquinone, to prevent further polymerization, was added to samples to reduce the mixture viscosity and hinder skin formation during evaporation. The monomer, methanol, and water were driven off by drying to a constant weight in a vacuum oven at 60°C. The dried polymer was weighed to calculate instantaneous monomer conversion, based on a simple mass balance equation. The results were occasionally checked by a chromatography method.

Particle Size

Photon correlation spectroscopy (PCS) or quasi-light-scattering (QLLS) and transmission electron microscopy (TEM) techniques were used for particle-size measurement. The details were given elsewhere.¹² UV crosslinking was used for polymer hardening when TEM was used. Particles, 1000–1500, were counted to give a statistical satisfactory result; a larger number of particles was counted for the latexes with wider size distribution.

Number of Particles

The number of particles, N_p , is given by

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

where D_v is the volume-average diameter of the particles; M , the amount of monomer fed by time t ; and x_i , the instantaneous conversion. TEM provides the complete distribution data from which D_v can be calculated. However, the PCS method gives a z -average diameter which is larger than the volume average. The application of the z -average to the above equation causes an underestimation of N_p . The methodology for converting the z -average size to the volume-average diameter was given elsewhere.¹²

Monomer Concentration in Polymer Particles

This can be calculated using the following expressions:

$$M_p = (1 - x_{cr})/(1 - x_{cr} + x_{cr}\rho_m/\rho_p)M_w \quad x_i \leq x_{cr} \quad (2)$$

$$M_p = (1 - x_i)/(1 - x_i + x_i\rho_m/\rho_p)M_w \quad x_i > x_{cr} \quad (3)$$

where M_w is molecular weight of the monomer; ρ_p and ρ_m , the density of polymer and monomer, which were taken as 0.869, and 1.026 g/cc, respectively; and x_{cr} , the conversion at which for a BA batch emulsion polymerization the transition from interval II to interval III occurs. x_{cr} is found from the kinetic studies to be 0.45.¹³ No allowance is made for BA dissolved in the aqueous phase during interval III, since BA solubility in the water phase is low. All surface tension measurements were made using a Du nouy ring tensiometer at room temperature.

RESULTS

M-Add Semibatch Process

Four sets of experiments were designed to investigate the effects of monomer distribution between the initial charge and the feed on the kinetics of M -add semibatch emulsion polymerization of BA. These sets are labeled as sets 1–4. $(R/F)_M$ is the weight of the monomer initially placed in the reactor divided by the whole monomer weight in the feed recipe. $(R/F)_M = 0$ means that no monomer was initially placed in the reactor, and $(R/F)_M = 1.0$ means that all the mono-

mer was placed in the initial charge, which is identical to a batch operation. The effects of $(R/F)_M$ for the M -add process were investigated at three different overall SLS concentrations and two M feed rates. The monomer distribution ratio varied between 0 and 0.40. Sets 2–4 were carried out using a M feed rate of 185 g/h and SLS loadings of 0.125, 1.25, and 5.0 g, respectively. Set 1 was performed using 5.0 g of SLS, but at a higher feed rate: 385 g/h. Set 5 was performed using the ME -add semibatch process. All runs are listed in Table I.

Figures 1 and 2 demonstrate overall and instantaneous conversions versus time for two sets of experiments. The polymerization reactions start with the monomer present in the initial charge. As the reaction proceeds during the seeding batch period, a high conversion is reached. When the monomer addition period starts, the rate of polymerization varies depending on the free monomer in the reaction mixture. The x_i showed some oscillations for the lower $(R/F)_M$ ratios before approaching the steady-state value: x_{ss} . For all runs, a small increase in the steady-state rate of reaction was observed with decreasing $(R/F)_M$. Figure 3 shows a typical variation in M_p with conversion for the experiments using 1.25 g of SLS and a feed rate of 185 g/h (set 2). The M_p showed some oscillations for the lowest $(R/F)_M$ ratio before approaching the steady-state value. Generally, the variation in M_p with time can be inferred from the x_i-t curves.

Figure 4 shows the evolution of particle size for set 1. For almost all $(R/F)_M$ ratios studied, a small decrease in the average particle size in the initial stage of reaction is observed. The number of particles versus overall conversion and with different monomer distribution ratios for the same set are shown in Figure 5. A larger number of polymer particles is obtained for the lower $(R/F)_M$ ratios. As is clear from Figure 5, particle nucleation stops at the earlier conversion for $(R/F)_M = 40$ and 20%, while it continues to higher conversions for $(R/F)_M = 5\%$. Figure 6 shows the variation in the number of particles with overall conversion for the experiments using a feed rate of 185.0 g/h and SLS loadings of 5.0 and 1.25 g (sets 2 and 3). The rate of particle formation is definitely enhanced with increasing SLS concentration, especially if no monomer is initially present in the reactor. For an SLS loading of 1.25 g, the number of particles only slightly increased within an eightfold increase in the $(R/F)_M$ ratio.

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

Runs	Feed Rate (g/h)	Charge (g)					Feed (g)				
		BA	DDI	SLS	KPS	SBc	BA	DDI	SLS	KPS	SBc
Set 1											
1	385	100	500	5.0	0.27	0.27	150	—	—	—	—
2	385	50	500	5.0	0.27	0.27	200	—	—	—	—
3	385	25	500	5.0	0.27	0.27	225	—	—	—	—
4	385	12.5	500	5.0	0.27	0.27	237.5	—	—	—	—
Set 2											
5	185	50	500	5.0	0.27	0.27	200	—	—	—	—
6	185	0	500	5.0	0.27	0.27	250	—	—	—	—
Set 3											
7	185	100	500	1.25	0.27	0.27	150	—	—	—	—
8	185	50	500	1.25	0.27	0.27	200	—	—	—	—
9	185	25	500	1.25	0.27	0.27	225	—	—	—	—
10	185	12.5	500	1.25	0.27	0.27	237.5	—	—	—	—
Set 4											
11	185	100	500	0.125	0.27	0.27	150	—	—	—	—
12	185	50	500	0.125	0.27	0.27	200	—	—	—	—
13	185	0	500	0.125	0.27	0.27	250	—	—	—	—
Set 5											
14	185	25	100	1.0	0.054	0.054	225	400	4.0	0.216	0.216
15	185	0	100	1.0	0.054	0.054	250	400	4.0	0.216	0.216

Figure 7 shows the particle-size distribution (PSD) of the final latexes for the individual runs of set 1. Figures 8 and 9 show the PSD of the final latexes for sets 1 and 3, collectively. The particle-size averages obtained by calibrated TEM were in agreement with those obtained from PCS. The particle-size data are given in Table II. The PSD

of the final latexes became broader as $(R/F)_M$ decreased. The PSD curves present a negative skewness which increased with decreasing $(R/F)_M$ ratio.

ME-Add Semibatch Process

Two experiments were carried out to study the effect of $(R/F)_M$ on the kinetic features. For both

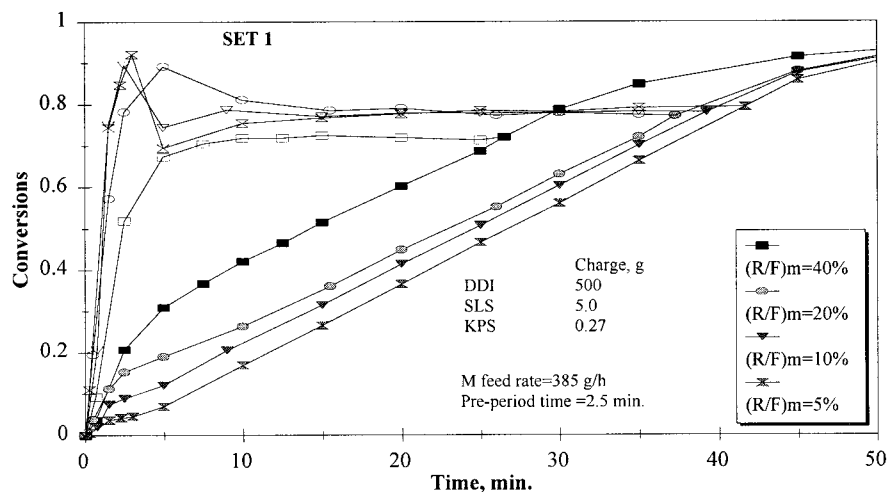


Figure 1 Time evolution of overall and instantaneous conversion for different monomer distribution ratios using 5.0 g SLS in the initial charge (filled symbols and open symbols show overall and instantaneous conversions, respectively).

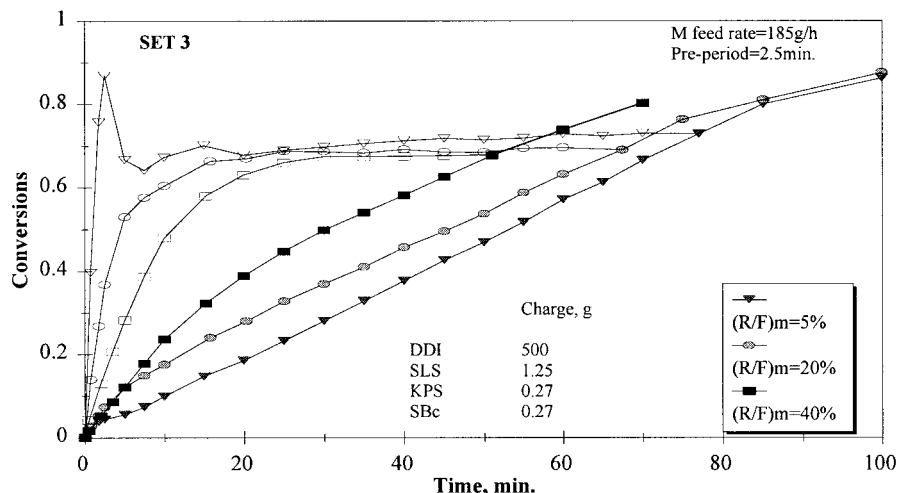


Figure 2 Time evolution of overall conversion (filled symbols) and instantaneous conversion (empty symbols) for different $(R/F)_M$ ratios using 1.25 g SLS in the initial charge.

runs, 20% of SLS, KPS, SBc, and DDI were initially charged to the reactor. For the first run, 20% of the monomer was initially placed in the reactor, while the second run was started with no monomer in the initial charge. The balance of the components were fed to the reactor at a constant monomer rate of 185 g/h.

Figure 10 compares the time evolution of conversions for the two monomer distribution ratios of $(R/F)_M = 10$ and 0.0 wt %. A higher initial rate of polymerization was obtained for $(R/F)_M = 10$ wt % compared with that from $(R/F)_M = 0.0$ wt %. The steady-state rate of polymerization (SSRP) increased with decreasing monomer charge. The

corresponding sample micrographs of final latexes are given in Figure 11. The presence of the monomer in the initial charge led to the formation of a smaller number of particles, as shown in Table III. The PSD curve indicates that for the run with the initial monomer charge secondary nucleation occurred and a bimodal PSD was obtained, as shown in Figure 12. The second peak at the higher size is indicative of particle nucleation in the beginning of the reaction. The first peak at the lower size represents secondary particle nucleation. The bimodal distributions can be represented as the sum of the two monomodal distributions if the diameters about which measured

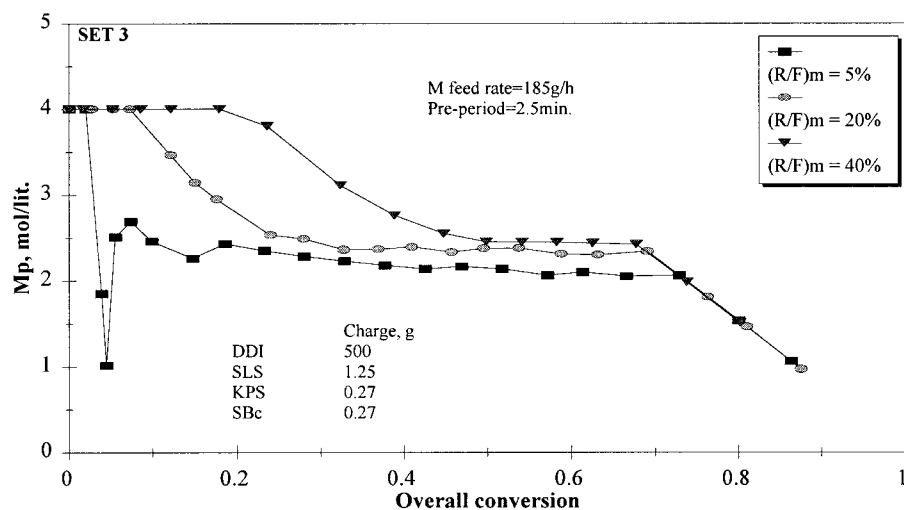


Figure 3 Monomer concentration in polymer particles versus overall conversion for different $(R/F)_M$ ratios using 1.25 g SLS in the initial charge.

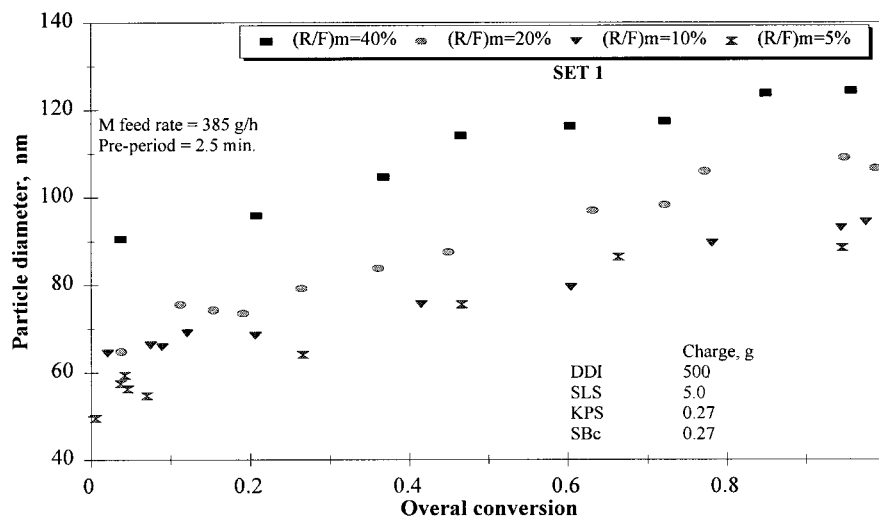


Figure 4 Average unswollen particle diameter versus overall conversion for different monomer distribution ratios using 5.0 g SLS in the initial charge.

values are grouped are quite different. This could be done for run 14, and the particle-size averages and polydispersities are given in Table III.

DISCUSSION

Particle Formation

In intervals I and II of a batch process, the monomer droplets act as reservoirs of the monomer. The monomer diffuses from the droplets to the locus of polymerization with the rate controlled by the free-radical propagation in the particles. Hence, a batch emulsion polymerization in inter-

val II may be inherently considered as a semi-batch process, a flooded one, in which the monomer is fed to the polymer particles from droplets. This is similar to the pumping of the monomer from an external reservoir to the reaction mixture with a rate that keeps particles saturated with the monomer. Under such conditions, particle nucleation occurs at monomer-flooded conditions. It has been reported before that particle nucleation in a monomer-flooded semibatch process resembles that of batch process.³ Krackler and Naidus² first explained reduced particle growth in a semi-batch emulsion polymerization reactor and introduced the concept of monomer-starved particle

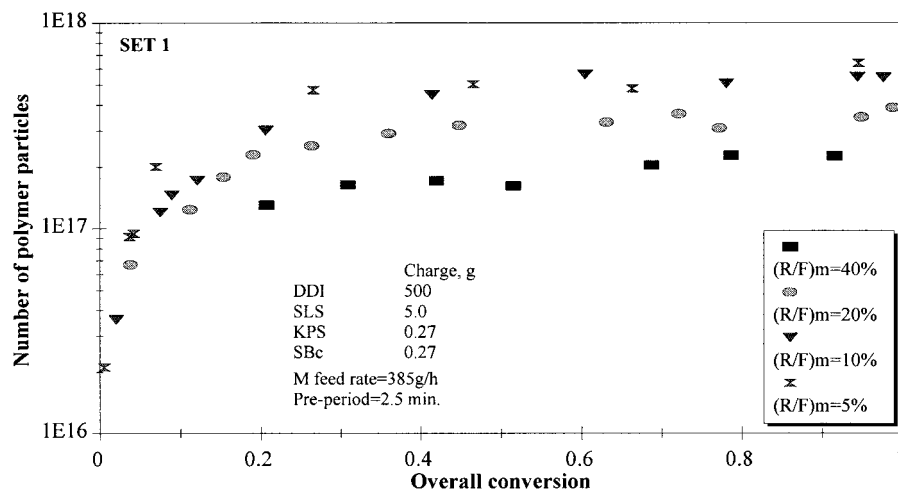


Figure 5 Particle number versus overall conversion for different $(R/F)_M$ ratios using 5.0 g SLS in the initial charge.

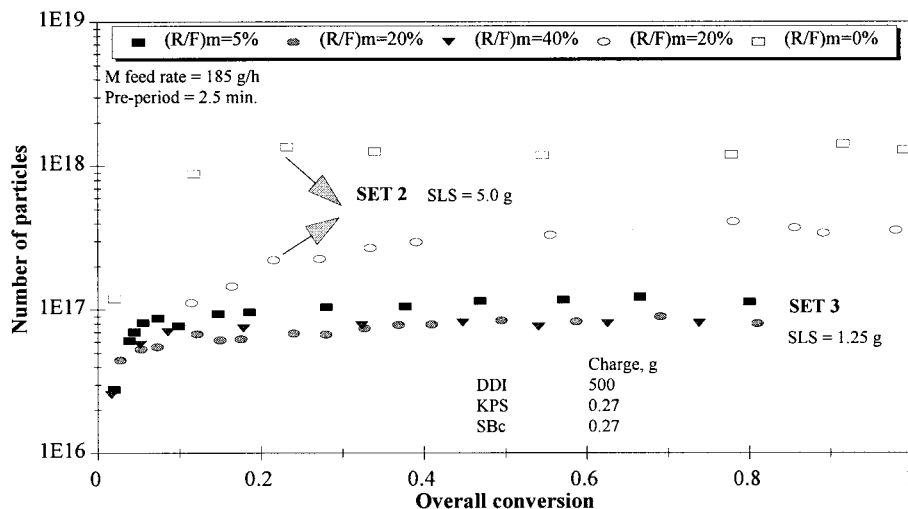


Figure 6 Particle number versus overall conversion for different $(R/F)_M$ ratios using 5.0 and 1.25 g of SLS and monomer feed rate of 185.0 g/h monomer feed rate (filled symbols and open symbols are for SLS loadings of 1.25, and 5.0 g, respectively).

formation. They showed that for semibatch emulsion polymerization particle nucleation at monomer-starved conditions can lead to formation of a larger number of polymer particles, compared with that from the equivalent batch process. The effect of a reduced growth rate on the number of particles can be best explained by the correlation developed by Smith and Ewart.⁶ For particle formation in Case II kinetics, they showed that

$$N_p = k(I_0/\mu)^{0.40}(\alpha_s S_0)^{0.60} \quad (4)$$

where k is a numerical constant; $\mu = dv_p/dt$, the volumetric growth rate per particle in interval I ; α_s , the adsorption area occupied by a molecule of an emulsifier on the surface of polymer particles; and S_0 , the amount of emulsifier forming micelles per unit volume of water.

It is clear from the above equation that the number of polymer particles is inversely proportional to the volume growth rate of polymer particles during nucleation. At monomer-flooded conditions, μ is constant and thermodynamically controlled at its maximum level and, hence, the smallest number of particles are formed. By using an M -add semibatch policy at monomer-starved conditions, it is possible to reduce the particle growth rate and increase the number of particles. It should be noted that in a monomer-starved semibatch operation using a constant monomer feed rate μ is not constant if particle formation occurs extensively. Therefore, the above equation cannot be used quantitatively for predicting the number of particles.

For an M -add semibatch process with a fixed recipe, the monomer-distribution ratio is the key variable because it determines the regime of particle formation. In fact, by varying the monomer initial charge, the contribution of monomer-flooded and monomer-starved nucleations to the whole nucleation process will be varied. The presence of a sufficient amount of monomer in the initial charge causes particle formation to occur at monomer-flooded conditions where the particle growth rate is a maximum. A low amount of monomer in the initial charge will drive the system to monomer-starved conditions where the particle growth rate is controlled by the rate of monomer addition and where more particles might be formed. Figure 3 shows such a variation in conditions with the initial monomer charge. For the run with lowest monomer charge, monomer concentration soon drops from the saturation value and monomer-starved conditions prevail. For the higher monomer charge, the onset of monomer-starved conditions is delayed longer. For any monomer-fed semibatch process, there is a threshold monomer concentration M_{cr} or monomer/water ratio, $(M/W)_{cr}$, above which the monomer present in the reactor charge is sufficient to consume all emulsifier micelles through nucleation; nucleation occurs through a monomer-flooded mechanism.¹³

Two scenarios exist: (1) $M_0 \geq M_{cr}$. If a semibatch process is operated so that particle nucleation is limited to the seeding batch, particle formation occurs under monomer-flooded conditions

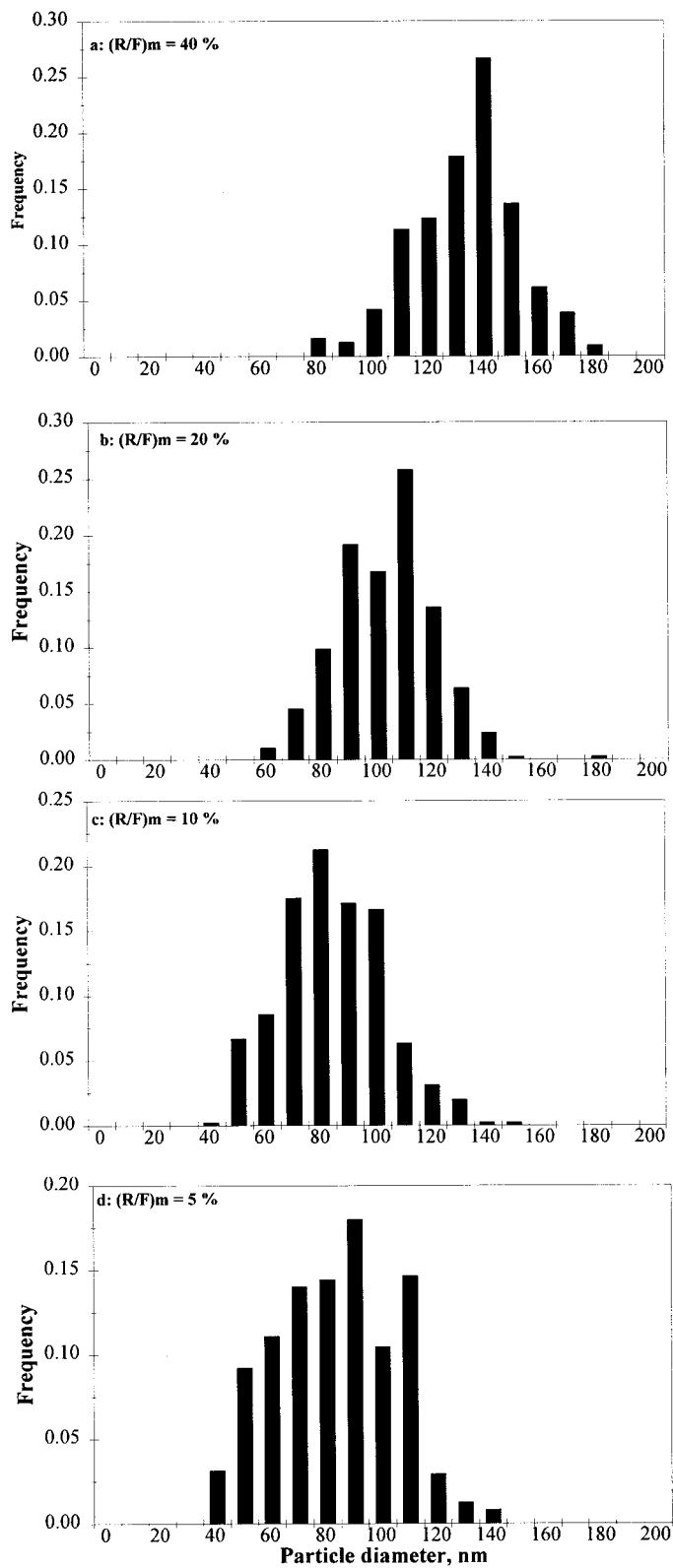


Figure 7 Variation in PSD of final latexes with monomer distribution ratio using 5.0 g of SLS in the initial charge; $(R/F)_M =$ (a) 40%, (b) 20%, (c) 10%, and (d) 5%.

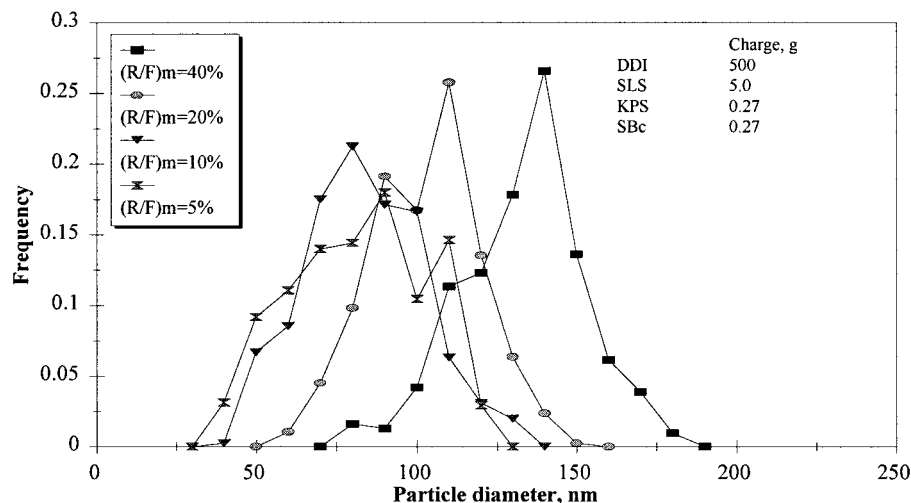


Figure 8 Variation in PSD of final polymer particles with monomer distribution ratio using 5.0 g of SLS in the initial charge.

and particles undergo growth in the subsequent stage and the number of particles becomes independent of M_0 and the feed rate. This condition can be achieved if a high initial value for M/E is used. (2) $M_0 < M_{cr}$. For such a system, the initial monomer charge is not enough to consume all emulsifier molecules and free emulsifier micelles remain in the reaction mixture when monomer feeding starts. The particle nucleation proceeds both during the seeding batch and the feeding stages, and, hence, its rate is influenced by both the rate of monomer addition and seeding batch conditions.

It can be concluded that in a semibatch process with M feed particle nucleation might be similar to a batch process if $M_0 > M_{cr}$. The results re-

ported in our previous publication¹³ for BA batch emulsion polymerization indicate that the approximate critical monomer concentration for SLS concentrations of 10 and 2.50 g/L at the conditions used in this study are $M_0 = 200$ and 25 g/L, respectively. Since the overall monomer/water ratio used in this study was kept constant at $M/W = 1/2$, the corresponding critical monomer-distribution ratios, $(R/F)_{M_{cr}}$, are 0.40 and 0.05, respectively. The $(R/F)_{M_{cr}}$ for each set is shown by bars in Figure 13, from which it is observed that for SLS concentrations of 10 and 2.50 g/L the number of particles increases with decreasing $(R/F)_M$ ratio if $(R/F)_M < (R/F)_{M_{cr}}$. In Figure 13, the number of particles for corresponding batch operations with overall $M/W = 1/2$, $(R/F)_M = 1.0$, are

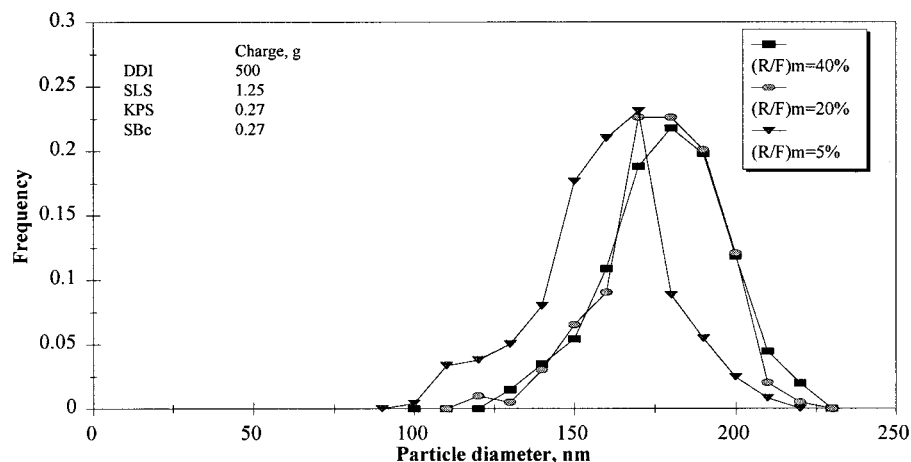


Figure 9 Variation in PSD of final polymer particles with monomer distribution ratio using 1.25 g of SLS in the initial charge.

Table II Number (D_n)-, Weight (D_w)-, Volume (D_v)-, and Intensity (D_I)-Average Diameters and PDI Obtained by Calibrated TEM and Average Diameter (D_z) Obtained by PCS of Final Latexes

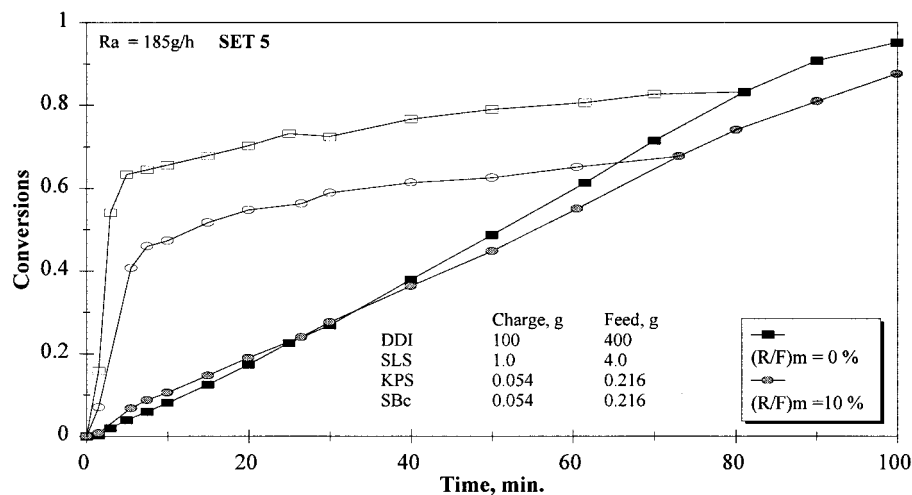
Run No.	Variable (R/F) _M (%)	X_f^a (%)	PCS (D_z (nm))	TEM (nm)				
				D_n	D_{vol}	D_w	D_I	PDI
Set 1								
1	40	96.5	138.3	128.0	130.9	136.2	139.8	1.06
2	20	98.8	118.6	99.0	100.6	106.6	111.2	1.08
3	10	97.7	104.9	79.1	83.3	92.1	97.6	1.17
4	5	97.8	98.3	77.2	83.3	94.1	100.1	1.22
Set 3								
7	40	88.0	189.1	175.3	177.2	181.0	186.9	1.03
8	20	87.6	186.8	171.0	173.1	176.8	181.7	1.03
9	10	87.1	182.3	—	—	—	—	—
10	5	86.4	163.6	155.1	158.0	163.1	170.0	1.05

^a Final conversion.

shown¹³ and compared with those of semibatch operations. It is seen from this figure that, practically, there is no difference in N_p between batch and semibatch operations for the higher range of the $(R/F)_M$ ratio, but the difference gradually develops with a decreasing $(R/F)_M$ ratio and becomes more appreciable at the low $(R/F)_M$ ratios. For high SLS concentration in the initial charge, 10.0 g/L, a continuous increase in the number of particles with decreasing $(R/F)_M$ was observed in which the slope of the $N_p - (R/F)_M$ curve increased with decreasing monomer feed rate. This is because particle nucleation continues to the feeding stage, where the rate of particle growth is controlled by the rate of monomer addition. Obvi-

ously, the larger number of particles is obtained for the lower monomer feed rate.

For the lowest SLS concentration studied, 0.25 g/L, N_p increases with a decreasing $(R/F)_M$ ratio in the whole range of $(R/F)_M$ studied. For this case, since $[S] < [S]_{CMC}$, there are no free emulsifier micelles, and particle nucleation occurs in a very short period of time through a homogeneous nucleation mechanism. For this condition, $(M/W)_{cr}$ can be assumed to be zero. Hence, the increase in N_p with the monomer initial charge cannot be explained in terms of M_{cr} , since the polymerizations occurred in monomer-flooded conditions where the number of particles is expected to be independent of the initial monomer

**Figure 10** Time evolution of overall (filled symbols) and instantaneous (empty symbols) conversions for different monomer distribution ratios $(R/F)_M$.

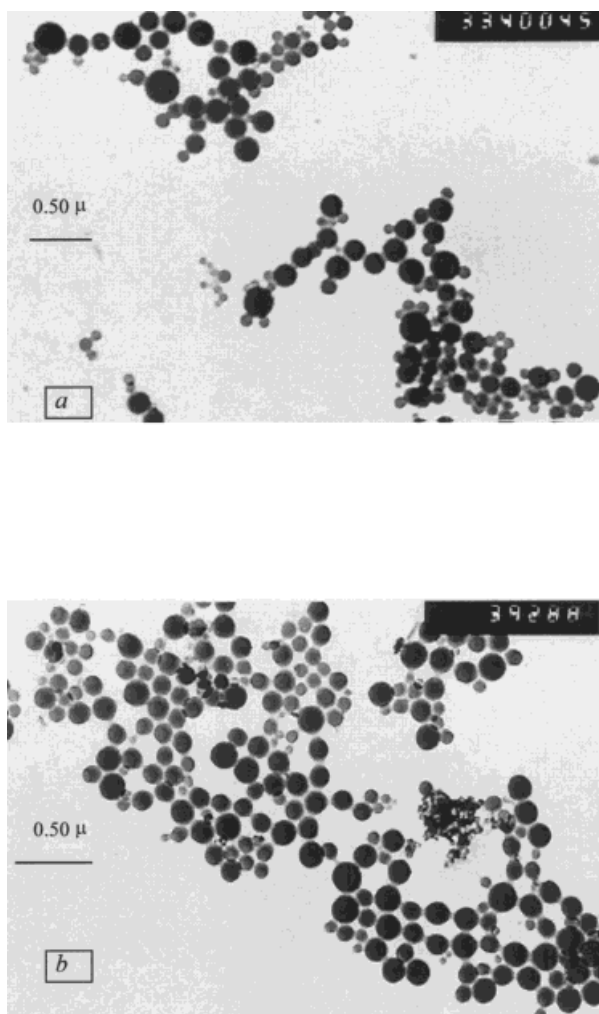


Figure 11 Micrographs for the final latexes from the runs using different monomer concentrations in the initial charge: (a) $(R/F)_M = 10\%$; (b) $(R/F)_M = 0\%$.

charge. For monomer-flooded semibatch processes using a low emulsifier charge, the following factors are important: First, during particle formation, with a lower number of monomer drop-

lets, fewer emulsifier molecules are adsorbed on the monomer droplets and more are available for particle formation. Second, during particle growth, particle coagulation is expected to be less operative at a lower SLS concentration with a smaller number of monomer droplets since they might accelerate particle coagulation by adsorbing free emulsifier molecules. These two factors could be less important for a system with a low M/E ratio where sufficient emulsifier molecules are available to outweigh emulsifier adsorption on the monomer droplets and to protect particles against coagulation. However, for a system with a low emulsifier concentration or high M/E ratio, these two factors must be taken into consideration, as is obvious from the results presented here (see Fig. 13). It was shown elsewhere¹³ that in the BA batch emulsion polymerization at low SLS concentration particle coagulation occurred in the course of the reaction. For low concentrations of SLS, the reproducibility of results was also not as good as that for stable systems. Comparison of the results obtained for a very high (M/E) ratio with those from the corresponding batch process¹³ shows that N_p is larger for semibatch processes for all $(R/F)_M$ values used here.

Semibatch emulsion processes with M feed provide a unique way to produce latexes with very fine particles. This can only be accomplished through suppressing the particle-growth rate by applying a very low monomer feed rate to a semibatch process with no or low initial monomer charge. Figure 6 shows that a large number of polymer particles, $2.60 \times 10^{18} \text{ L}^{-1}$, is formed when polymerization is carried out at highly monomer-starved conditions, high emulsifier concentration, and no monomer initial charge. The final particle size was almost 60 nm, which is much smaller than that of particles of conventional emulsion latexes. Due to continuous parti-

Table III 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 Monomer-Distribution Ratios

Run	$(R/F)_M$ (%)	PCS (nm) D_z	SEM (nm)										
			Overall Peak					Primary Peak			Secondary Peak		
			D_n	D_w	D_v	D_I	PDI	D_n	D_w	PDI	D_n	D_w	PDI
Set 5													
14	10	205	137	202	164	211	1.48	201	209	1.04	74	83	1.12
15	0	153	112	131	119	137	1.17	—	—	—	—	—	—

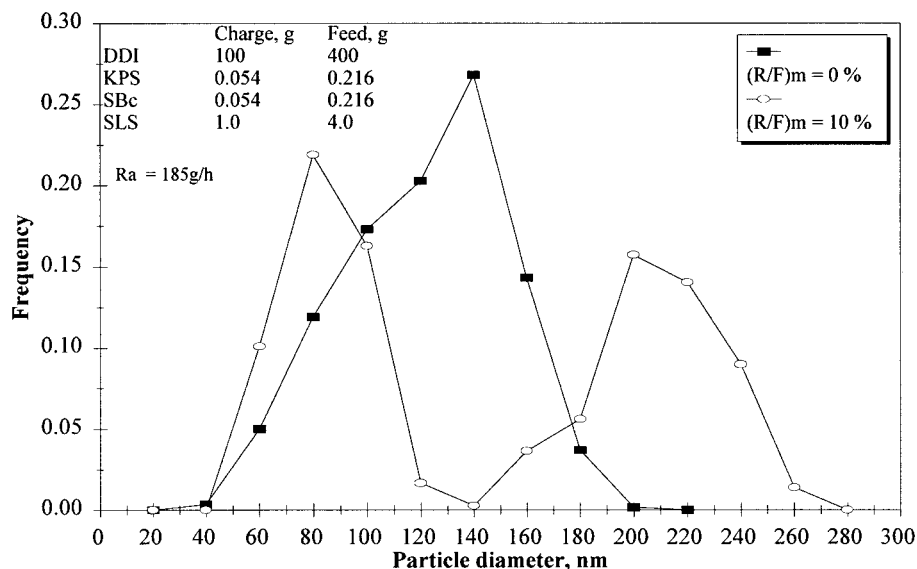


Figure 12 PSD curves for latexes with different monomer concentrations in the feed and 1.0 g of SLS in the initial charge.

cle formation and relatively small particle sizes, the viscosity of the latex increased with conversion so that mixing became very difficult as the reaction proceeded.

In semibatch processes, as the time span over which the particle nucleation occurred increases, the PSD of latexes is expected become broader.² Figure 9 confirms that in a semibatch emulsion polymerization using $M_0 > M_{cr}$ particle nucleation occurs at monomer-flooded conditions and is

independent of monomer charge, resulting in similar PSD curves for each $(R/F)_M$ value. In semibatch emulsion polymerization runs using $M_0 < M_{cr}$, particle nucleation starts from the seeding batch and continues to the feeding stage where more particles are formed. The period of particle nucleation increased with decreasing monomer feed rate and $(R/F)_M$ ratio. Correspondingly, a wider polydispersity index (PDI) was obtained for the lower $(R/F)_M$ ratio as depicted in Figures 8

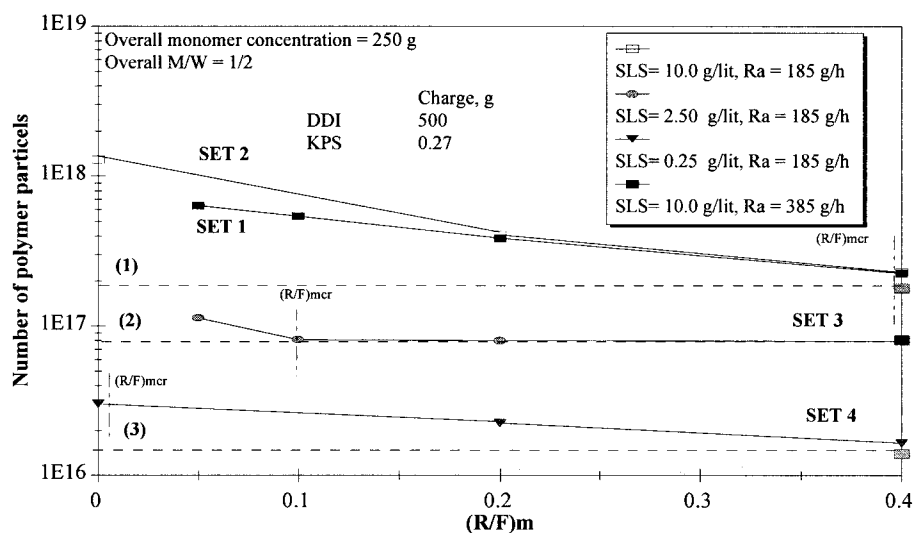


Figure 13 Total number of polymer particles as a function of monomer distribution ratio for different SLS concentrations and monomer feed rates. Dashed lines indicate number of particles obtained from corresponding batch operation using SLS concentration of (1) 10.0, (2) 2.5, and (3) 0.25 g/L.

Table IV Final Number of Particles, Steady-State Conversion, and Steady-State Radical Number for Different Runs

Variables	Sets								
	Set 1			Set 2			Set 3		
	Runs								
	1	2	3	4	5	6	7	8	9
R_a (g/h)	385	385	385	385	185	185	185	185	185
$(R/F)_M$ (%)	40.0	20.0	10.0	5.0	20.0	0	40.0	20.0	5.0
M_0^a (g)	100	50	25	12.5	50	0	100	50	12.5
SLS (g)	5.0	5.0	5.0	5.0	5.0	5.0	1.25	1.25	1.25
Results									
$N_p \times 10^{-17}$	2.3	3.9	5.4	6.4	3.5	12.9	0.80	0.80	1.1
x_{ss}^b	0.73	0.79	0.79	0.80	0.87	0.91	0.73	0.73	0.74
\bar{n}	0.15	0.12	0.09	0.08	0.12	0.05	0.21	0.21	0.16

^a M_{0cr} for sets 1–3 are 100, 100, and 25 g, respectively (based on a 0.500-L aqueous phase), which are equivalent to $(R/F)_{Mcr} = 40.0, 40.0,$ and 10.0% , correspondingly.

^b $x_{ss} = R_p/R_a$.

and 9 and Table II. The PDI of the final latexes from set 1 was, for example, 1.06 for $(R/F)_M = 40\%$ and 1.22 for $(R/F)_M = 5\%$, which shows an appreciable difference in the PSD of the latexes obtained.

Emerging peaks on the PSD curves from latexes using low $(R/F)_M$ ratios are observed in Figure 7. According to the classical theory of Smith and Ewart, the rate of particle nucleation is a decreasing function of time. This predicts a monomodal PSD for conventional batch emulsion polymerizations. In semibatch emulsion polymerization, particles formed during flooded conditions grow quickly. As the monomer concentration drops below its saturation value during the seeding batch, particle growth slows down while particle nucleation continues since excess emulsifier molecules exist in the reaction mixture, resulting in an emerging high population of small particles which manifests itself by a small peak in some region of PSD curves. The generation of new particles can be inferred from Figure 4, which shows that the average particle size stays virtually constant within 10–20% conversion while twice as much polymer is produced. The small peak in the PSD curves appears as M_0 is reduced below M_{cr} . Initially, the emerging small peak is indicative of monomer-starved nucleation and appears at the lower size range of the PSD curve, since a larger number of particles have formed through monomer-flooded conditions. As M_0 de-

creases, more particles are formed through monomer-starved nucleations and less are formed through monomer-flooded nucleation. This results in appearance of a small peak on the higher-size region of PSD curve, which is indicative of particles formed at monomer-flooded conditions. At a very low M_0 , particle formation occurs at monomer-starved conditions from the beginning, and as a result, no second peak on the PSD curves is expected. The occurrence of the emerging peak for low SLS concentration, 2.50 g/L, was not observed, possibly because most of the emulsifier micelles were depleted through monomer-flooded nucleation and only a small proportion of particles is formed during monomer addition, as given by N_p in Table IV.

The classification mentioned before is also valid for *ME*-add semibatch operation. Similarly, the presence of low monomer concentration in the initial charge will prolong the particle nucleation period and, hence, increase the number of particles if $M_0 < M_{cr}$. The conditions of the seeding batch in run 14 is such that $M_0 > M_{cr}$, so a short nucleation period was obtained. Obviously, for run 15 using $M_0 = 0$, particle nucleation occurred through monomer-starved nucleation and a large number of particles was formed, as shown in Table III. However, since in the *ME*-add process the emulsifier is continuously added to the reactor, secondary nucleation might occur. Application of a large amount of monomer charge in a semibatch

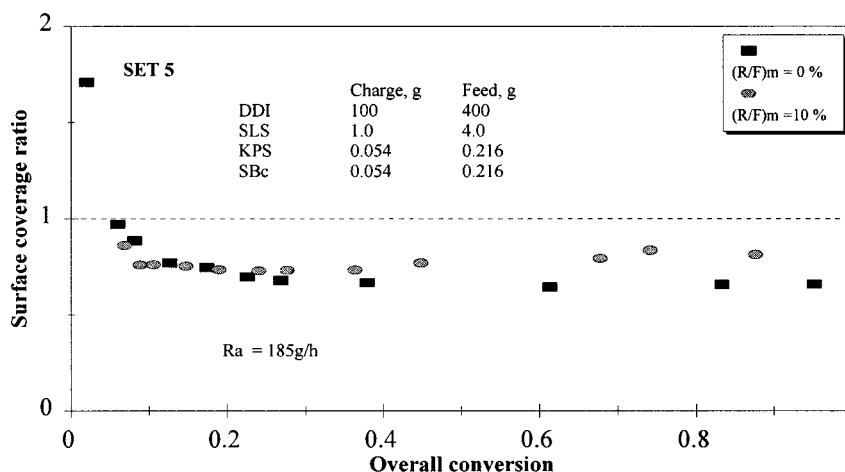


Figure 14 Surface coverage ratio versus overall conversion for different monomer distribution ratios $(R/F)_M$.

emulsion process with the monomer emulsion feed might increase the possibility of secondary nucleation, simply because it reduces the extent of primary nucleation. This is clearly manifested in the micrographs of the final latexes for the two *ME*-add runs, by a wide size distribution of particles obtained for the latex using the initial monomer charge. The occurrence of a bimodal PSD can be observed in Figure 12 for the run using monomer in the charge. A monomodal PSD, but with a wide polydispersity index (1.17), is obtained for the run with no monomer charge, which is indicative of a long nucleation period at monomer-starved conditions. A large particle surface area which developed, for this case, adsorbs most incoming emulsifier molecules and hinders secondary particle formation.

By monitoring the surface coverage of polymer particles with emulsifier molecules, an indication was obtained that secondary nucleation occurred through a homogeneous nucleation mechanism, because there was insufficient emulsifier to form micelles. It is known that PCS is not very sensitive to small particles and PCS measurements are not very accurate for polydisperse particles. However, it can provide an acceptable estimation of average particle size, if an appropriate correction is made.¹² Using the average particle size obtained by PCS and the total amount of emulsifier in the reaction mixture at time t , it is possible to estimate the surface coverage ratio of particles in the course of the reaction. The average particle surface coverage ratio is calculated as follows:

$$SC = N_a S_p a_s / \pi D_{ps}^2 N_p \quad (5)$$

where a_s is the area occupied by a emulsifier molecule on the surface of polymer particles, and D_{ps} , the average diameter of the swollen particles. The value obtained for a_s is 0.63 nm^2 .¹³ S_p is the amount of emulsifier adsorbed on the particles, which, for the present study, is assumed to be the total amount of the emulsifier. The unswollen particle sizes are directly obtained from PCS and TEM measurements. Using the saturation value of the monomer concentration in the particles, together with conversion in the reactor, it was possible to calculate the swollen or actual particle size.¹³ $SC \geq 100\%$ means that particles are fully covered by emulsifier molecules and excess micelles exist in the reaction mixture.

Figure 14 reveals that the surface coverage ratio of particles for the reaction using the initial monomer charge drops to a low value and then approaches the full coverage at the end of the reaction, while it stays practically constant for the run with no initial monomer charge. The variations of surface tension with time also correlate with particle formation (not shown here). A rather steep increase in the surface tension was observed in the course of the reaction if no monomer was present in the initial reactor charge. For $(R/F)_M = 10\%$, the surface tension levels off early in the reaction and shows a slight decrease in the later stage of the reaction. The low surface coverage of polymer particles with emulsifier molecules, as shown in Figure 14, and the high surface tension during feeding, which was in the range of 35.0–37.5 dyne/cm and above that of CMC value (29.0 dyne/cm), indicate that secondary nucleation occurred through homogeneous nucleation.

Rate of Polymerization

The steady-state rate of the polymerization was only slightly influenced by the initial monomer loading, despite a large variation in the number of polymer particles. For BA semibatch emulsion polymerization with M feed at the conditions similar to those used here, it was found that the steady-state average radical number per particle stays constant in the course of the reaction and that the steady-state rate of polymerization can be correlated with the rate of monomer addition through the equation $1/R_p = 1/K + 1/R_a$.¹² This requires that the steady-state value of x_i , x_{ss} , should be independent of the history of the transition period before a steady state is reached. This is verified in Figures 2 and 3, which show a practically constant x_{ss} (or M_p) was achieved for most monomer loadings studied. Only a slight increase in x_{ss} was observed with the monomer charge if it is associated with increase in the number of particles. The only exception is for the highest monomer charge which showed a larger M_p (smaller x_i), as shown in Figure 3. Results from steady-state polymerization for different conditions are given in Table IV.

The instantaneous conversion during the steady state is $x_{ss} = R_p/R_a$, and a higher x_{ss} is obtained for the higher rate of polymerization.¹² Obviously, a higher R_p/R_a would be expected for lower R_a , according to Wesseling's analysis.⁴ The decrease from $(R/F)_M = 0.20$ to 0.05 for the SLS concentration of 10 g/L and $R_a = 385$ g/h almost doubled the number of particles, while it had practically no effect on the rate of polymerization, as reflected in Table IV. The steady-state rates of polymerization obtained for all three sets (1, 2, and 3) show little dependence on the number of particles, which is in accord with Case 1 kinetics. This effect can be further analyzed by looking at the variation of the number of radicals per particles with the initial monomer charge. The average radical number can be simply obtained from the overall rate of reaction as

$$\bar{n} = R_p N_a / k_p M_p N_p \quad (6)$$

where k_p is the propagation rate constant, and N_a , Avagadro's number. It has been shown before that, for BA, k_p values reported in the literature are very spread out.^{14,15} Taking $k_p = 4900$ L mol⁻¹ sec⁻¹ at 50°C,¹⁴ the steady-state radical number, \bar{n}_{ss} , is calculated and shown in Table IV for most sets. M_p was obtained using Eq. (4) and the corresponding x_{ss} from Table IV. An appreciable difference in the radical number is observed

for the runs using different initial monomer concentrations. The radical number decreases markedly with monomer charge, if it is associated with increase in the number of particles. The steady-state radical number stays practically constant for the runs using $M_0 > M_{cr}$.

The results imply that the radical number is a decreasing function of the number of particles at a constant SLS concentration. However, some other complementary information regarding the dependence of the radical number on the number of particles can be obtained by cross examination of the runs from different sets. Table IV reveals that for runs 5 and 8, carried out at a monomer feed rate of 185 g/h and different emulsifier loadings of 5 and 1.25 g, a larger number of particles was obtained for the higher SLS loading. This is associated with an appreciable increase in R_p or x_{ss} . As discussed above, the number of particles was found to have a small effect on the steady-state rate of polymerization if variation in the number of particles is induced by altering the initial monomer loading. Thus, this provides an indication that SLS accelerates the rate of KPS decomposition in BA emulsion polymerization.

For the *ME*-add semibatch process, the presence of monomer in the initial charge causes a rapid consumption of monomer molecules and enhances the initial rate of polymerization, as depicted in Figure 10. Elimination of the monomer from the initial charge reduces the initial rate of polymerization, but increases the rate of particle nucleation at the cost of a lower rate of particle growth. The overall rate of polymerizations showed a constant increase in the course of the reaction, due to continuous addition of the initiator and emulsifier. As a result, no constant instantaneous conversion was observed for these runs during feeding.

The time variation of the polymerization rate and instantaneous conversion substantially varies with monomer concentration loadings. There is a time lag for any semibatch process, or transition time, before the system reaches steady-state conditions. Moritz¹¹ indicated that for *M*-add semibatch emulsion polymerization of vinyl acetate, when the initial monomer charge exceeded the solubility level (25 g/L), the reaction rate at once increased to the stationary value. The results obtained here show that (see Figs. 1 and 2), generally, the transition time is shorter for the lower initial monomer charge, at a constant monomer feed rate, since a smaller proportion of the monomer should react to reach the steady-state value of conversion (assuming that x_{ss} is not very dependent on N_p at the steady state). Fur-

thermore, the larger number of particles formed for the lower monomer charge (if $M_0 < M_{cr}$) will increase the initial rate of polymerization so that the steady-state value is reached sooner and, hence, the transition time is shortened. However, such a conclusion cannot be generalized. If a long preperiod time is used, or if the initial rate of polymerization is high, so that x_{ss} is exceeded before monomer addition starts, this rule might not apply. A full treatment of the transition time and its variation with the monomer charge will be given elsewhere.¹²

CONCLUSIONS

The initial monomer charge was found to have a substantial effect on the number of polymer particles formed in the semibatch emulsion polymerization of BA. By decreasing the monomer charge below its critical value, M_{cr} , the relative contribution of monomer-flooded and monomer-starved nucleations to the nucleation process will change. Monomer-starved nucleation enhances the rate of particle formation due to the reduced particle growth rate. As a result, a larger number of particles is obtained for a lower monomer concentration if $M_0 < M_{cr}$. The maximum number of particles can be obtained if polymerization starts at highly monomer-starved conditions with no monomer in the initial charge. For a fixed recipe, the semibatch process with M feed can produce a remarkably large number of particles compared with that from batch process. The transfer from monomer-flooded to monomer-starved nucleation is marked by the appearance of an emerging second peak on the PSD curves which moves with the initial monomer concentration. The initial monomer charge was found to affect the transient behavior of the rate of polymerization, while it did not practically affect the steady-state rate of polymerization and steady-state instantaneous conversion. The experimental results ob-

tained in this research work show that for BA emulsion polymerization the steady-state rate of the reaction is only slightly influenced by the number of particles if the variations in the number of particles are caused by changes in the monomer concentration in the initial charge. As a result, the steady-state radical number substantially decreased with an increasing number of polymer particles.

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