

# Study of Different Types of Monomer Emulsion Feedings to Semibatch Emulsion Polymerization Reactors

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**ABSTRACT:** Semibatch emulsion polymerization processes with a monomer emulsion feed are of great importance in both academia and industry. Monomer emulsion feeds can be applied to semibatch reactors using either a stream of an emulsified monomer or two streams of a neat monomer feed and an aqueous solution of an emulsifier. The effect of the feeding policy on the rate of polymerization and on the secondary particle formation was studied for a seeded semibatch emulsion polymerization of styrene. When a single-stream monomer emulsion feed is applied to a semibatch process, the monomer-swollen micelles formed in the feed might become the locus of initiation upon entering the reaction vessel. Under the conditions of this study, the application of monomer emulsion feed in either one stream or two streams did not result in secondary particle formation. The incoming monomer-swollen micelles were disintegrated to supply emulsifier molecules for the stability of growing particles, before they can capture radicals and become polymer particles. The rate of polymerization was found to be independent of the way that the monomer emulsion feed is added. In the absence of nitrogen, the rate of polymerization decreased more appreciably for the monomer emulsion feed, due to the oxygen dissolved in the emulsified monomer. The number of particles, however, was not affected by the purging policy. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2472–2477, 2001

**Key words:** particle nucleation; emulsion polymerization; micelles; semibatch reactor; nitrogen purging

## INTRODUCTION

Semibatch emulsion polymerizations can be carried out using different feed types. Two main types of feeds have received the greatest attention<sup>1</sup>: neat monomer feed and monomer emulsion feed. Monomer emulsion feeds may vary between an emulsified monomer solution<sup>2</sup> and an emulsion recipe containing all ingredients.<sup>3</sup> The major components of monomer emulsion feeds are a

monomer(s), an emulsifier, and water. But they may contain other ingredients such as an initiator and a buffer. This gives a wide variety of properties to the monomer emulsion feeds that strongly affects the overall features of polymerization reactions.

While in the monomer addition technique there is not much variety in the feeding method, there are several ways of applying monomer emulsion feeds to a reaction mixture. Monomer emulsion feeds may be added to polymerization reactors with either two separate lines of a monomer and an aqueous solution of an emulsifier and an initiator (M & E feed)<sup>4–7</sup> or with a single stream of a monomer emulsion (ME feed). The

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application of two streams of an emulsified monomer solution and an aqueous solution of an initiator was also reported.<sup>8</sup> While these types of feeds are similar in terms of composition, they might, however, be different in properties.

The two streams of a neat monomer feed and an aqueous solution of initiator and an emulsifier are usually used, in academia, to avoid problems with phase separation of the two phases in the tube lines of dosing pumps. On the other hand, in industry, the single-stream monomer emulsion feed is widely used. It is common in research laboratories to apply nitrogen blanketing over polymerization reactors and emulsification vessels. The application of nitrogen purging, however, is very limited in industry due to its high cost.

The differences between single-stream and double-stream monomer emulsion feeds can be discussed in terms of monomer droplets and micelles: (1) When emulsification occurs by mixing a monomer and an aqueous solution of an emulsifier, monomer droplets are formed. However, for a double-stream feed, monomer droplets are formed upon entering into the reaction vessel. In agitated liquid-liquid dispersion systems, there is a transition time during which the size of the drops is exponentially reduced until a steady drop size is reached.<sup>9</sup> It can be assumed that the size of the monomer droplets reaches the steady-state value during the emulsification in the feed tank. Thus, for a single-stream monomer emulsion feed, the size of the entering monomer droplets into the reactor is much smaller than that of droplets formed in the reaction vessel if a neat monomer is added to the reactor. The extent of variations in the size of monomer droplets also depends on the polymerization conditions and the amount of free emulsifier in the reaction mixture. Generally, the monomer droplets are not considered to be a significant locus of polymerization because of their small surface area compared with that of monomer-swollen micelles. The variation in the size of droplets in the context of this study, therefore, is not expected to affect the polymerization kinetics. The monomer droplets formed in the monomer emulsions can contribute to particle formation if their sizes are reduced to a very small value so that they can compete with polymer particles for adsorbing radicals.<sup>10</sup> (2) When the aqueous solution of an emulsifier and a monomer are fed into reactors with two streams, micelles are not swollen with the monomer. The diffusion of the monomer into micelles is a slow process. It is possible that micelles break up quickly in the reaction

**Table I** Recipe Used for the Styrene Seeded Semibatch Emulsion Polymerization

Reactor Charge	Initial Charge (g)	Feed (g)
Seed latex	75.0	—
Styrene	2.5	100
DDI	250	200
SLS	—	0.50
KPS	0.54	—
SBC	0.54	—

vessel to cause the emulsifier molecules to diffuse into the growing particles in order to stabilize them, before the monomer can diffuse into them. When a monomer is present in micelles, their lifetime is very much increased<sup>11</sup> and the rate of breakup of the micelles decreases, as micelles become richer in the monomer. Brooks<sup>12</sup> stated that although the rate of micelle breakup is fast it is not instantaneous. It might be possible that incoming micelles capture radicals from the aqueous phase before they break up. The same mechanism may influence particle nucleation in semibatch reactors. No reports have been devoted to this issue in the literature. In this research, we studied the application of a single-stream monomer emulsion feed and a double-stream feed composed of a monomer and an aqueous solution of an emulsifier to the seeded semibatch emulsion polymerization of styrene.

## EXPERIMENTAL

The reagent styrene, supplied by Aldrich (Gillingham, UK), was further purified by distillation at a reduced pressure to remove the inhibitor. Sodium lauryl sulfate (SLS) (>99.0% purity), potassium persulfate (KPS), and sodium bicarbonate (SBC) were obtained from Sigma (Gillingham, UK), Merck (Poole, UK), and Panreac (Barcelona, Spain), respectively, and were used as received. Polymerizations were carried out at  $70 \pm 0.50^\circ\text{C}$  in a 1.0-L jacketed glass reactor with the recipe given in Table I. The experimental setup is similar to the procedure explained elsewhere.<sup>7</sup> The stirrer rate was kept constant at 350 rpm. The reactor was initially charged with all the required components with the exception of the initiator. Nitrogen purging of the reaction mixtures was carried out for all experiments according to the

conventional routines. The start of the feeding and the addition of the initial initiator charge to the reactor occurred simultaneously. The feed components were introduced into the reactor using a dosing pump with two heads. The total feeding time for all the components in the feed was 2.0 h, which gives the total feeding rate of 150 g/h for the monomer emulsion feed. This corresponds to monomer and aqueous solution feed rates of 50 and 100 g/h, respectively. The monomer emulsion was prepared in an emulsification stirred tank and kept stirred during feeding. The tube line for feeding the monomer emulsion was kept very short (50 cm) to hinder phase separation during the feeding.

When a seeded polymerization starts with no initial monomer present in the reactor, the incoming monomer molecules first have to diffuse into polymer particles in order to react. The monomer diffusion into polymer particles of styrene, with a  $T_g$  of 104°C, is a slow process. To eliminate this effect, we added 2.5 g of styrene to the seed latex, weighed for the experiment, and kept the latex overnight to assure that the particles are plasticized with the styrene monomer. The critical micellar concentration (CMC) of SLS in distilled water (DW) was found to be 1.75 g/L (1.0 g/L in the aqueous phase at the polymerization conditions), which is lower than the SLS concentration in the feed (2.50 g/L). This indicates that micelles are formed in the aqueous phase of the feed. Sampling was carried out at the desired time interval by removing an aliquot of 1–2 g latex with a hypodermic syringe. The monomer conversion in the reactor was measured gravimetrically. The particle sizes of the final latexes were determined with a transmission electron microscope (TEM). From each sample, several micrographs were prepared to allow reliable particle-size distribution (PSD) measurements. The magnification of TEM was calibrated with a series of diffraction grating replicas. The details for calculation of the polydispersity index (PDI) and other particle-diameter averages are similar to those used elsewhere.<sup>7</sup> Photon correlation spectroscopy (PCS or quasi-elastic light scattering, QELS) was also used for estimation of particle sizes. The light-scattering measurements (SEMATEch) were carried out at a 90° angle. No correction was made on the particle size obtained by PCS, because particles were monodisperse.

Two series of experiments were conducted: In series W, which was carried out with purging the feeds (by nitrogen) during feeding, three runs

were performed. In run W1, all components were fed into the reactor via a single stream of the monomer emulsion feed (ME feed). In run W2-a, the components were fed into the reactor via two streams of the monomer feed and an aqueous solution of the emulsifier (M & E feed). In run W2-b, two streams were used. However, the stream containing the aqueous solution of the emulsifier was saturated with the monomer so that micelles were swollen with the monomer (modified M & E feed). This run seems to be equivalent to run W1. In series WO, two experiments, similar to W1 and W2, were conducted with the difference that the feed tank(s) was not kept under the blanket of nitrogen during feeding (the reaction vessel was continuously purged with nitrogen during feeding). They were labeled as WO1 and WO2, respectively.

### Seed Preparation

The seed was prepared via batch emulsion polymerization of styrene with a recipe as follows: 1300 g of distilled deionized water (DDI), 700 g of styrene, 10.0 g of SLS, 2.0 g of KPS, and 2.0 g of SBC. The seed preparation was carried out nonisothermally, starting from the initial temperature of 82.0°C and reaching the maximum temperature of 95.0°C. The polymerization reaction was almost complete after 2 h. The reaction vessel was kept at 82.0°C for 10 h to decompose the initiator. The latex was then dialyzed at room temperature for 5 days in dialysis tubing, with daily changes of the DDI. This procedure gives particles with a number-average diameter of 119 nm (measured by TEM). The polydispersity of the seed latex was 1.012.

## RESULTS AND DISCUSSION

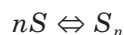
Table II shows particle-size data of the final latexes measured by calibrated TEM and PCS. The size of particles measured by PCS was slightly greater than that obtained by TEM. It can be seen from this table that the average diameters of particles obtained by all five runs do not show appreciable differences. The slight variations in the size of the final particles originate from the difference in the final conversion of the latexes. Figure 1 shows typical micrographs, prepared with a TEM, for particles from run W1 and W2-a. It is evident, from the micrographs, that no secondary particles were formed during the feeding for all runs. This

**Table II** Number ( $D_n$ )-, Weight ( $D_w$ )- and  $z(D_z)$ -Average Diameters and PDI of Final Latexes Obtained by Calibrated TEM and PCS

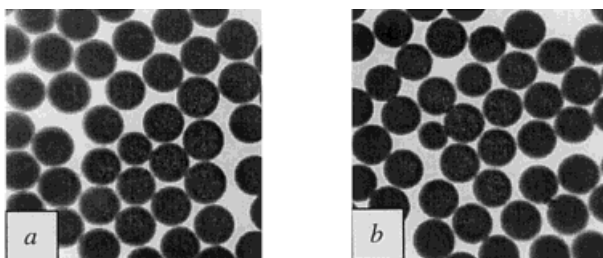
Series	Label	PCS $D_z$ (nm)	TEM		
			$D_n$ (nm)	$D_w$ (nm)	PDI
With N <sub>2</sub> purging					
ME feed	W1	220	208	211	1.012
M & E feed	W2-a	219	211	214	1.011
Modified M & E feed	W2-b	223	209	210	1.005
Without N <sub>2</sub> purging					
ME feed	WO1	215	205	206	1.004
M & E feed	WO2	216	206	208	1.010

indicates that the rate of micelle breakup is very fast so that they disintegrate as soon as they enter the reaction vessel. The presence of a monomer inside micelles (in single-stream monomer emulsion feed), which prolongs the lifetime of micelles, did not lead to secondary nucleation. It can be concluded that the rate of micelle breakup is much higher than is the rate of radical capture by micelles. The elimination of N<sub>2</sub> purging did not result in any variation in the population of particles. The results obtained imply that, under the conditions studied, the number of particles is independent of the way that the feeds are added to the reactor.

Micelles can be considered as dynamic entities. If we represent the amphiphatic species of the emulsifier by  $S$ , then the clustering process of emulsifier molecules can be described by the reaction



In fact, the above reaction should be written as a sequence of stepwise additions of emulsifier mol-



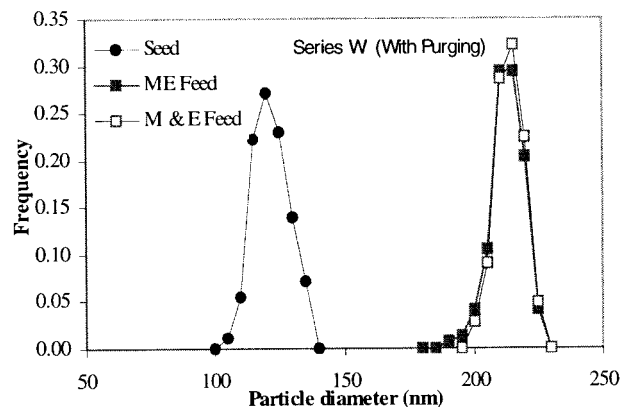
0.2 micron

**Figure 1** Micrographs of the final latexes prepared with N<sub>2</sub> purging with (a) double-stream M & E feed (run W2-a) and (b) single-stream ME feed (run W1).

ecules to the cluster until the aggregation number  $n$  is reached. Increasing the surfactant concentration should shift the equilibrium in the above equation to the right. Thus, the lifetime of micelles depends on the emulsifier concentration in the aqueous phase. As the emulsifier concentration increases above the CMC, the lifetime of the micelles increases. On the other hand, the more the aqueous phase of the reacting latex becomes emulsifier-starved (below the CMC), the faster is the rate of micelle breakup when the ME enters the emulsion reaction mixture. We do not have any estimation of the emulsifier concentration in the initial reactor charge, because it is known that dialysis cannot remove all the emulsifier molecules adsorbed on the particles in such a short period of time (5 days). Also, we did not perform soap titration to find the remaining emulsifier molecules on the surface of the seed particles. It is possible, however, that if the emulsifier concentration in the reaction vessel reaches the vicinity of the CMC, some secondary nucleation occurs because of the prolonged lifetime of the micelles.

Figure 2 compares the PSD of the seed particles with typical PSDs of grown particles from runs W1 and W2-a. No appreciable variation in size distribution of the particles was observed. The breadth of the distribution of the particles slightly decreased during feeding. The standard deviation of seed particles is 30 nm, which decreased to 21 nm after addition of the monomer emulsion feed. Liotta et al. studied the comparative growth of polymer particles in monomer-starved semibatch emulsion polymerization of styrene.<sup>13</sup> Their results showed that the order of volume growth can be controlled by the PSD of





**Figure 2** Comparison of size distribution of seed particles with those of the latexes from runs W1 and W2-a.

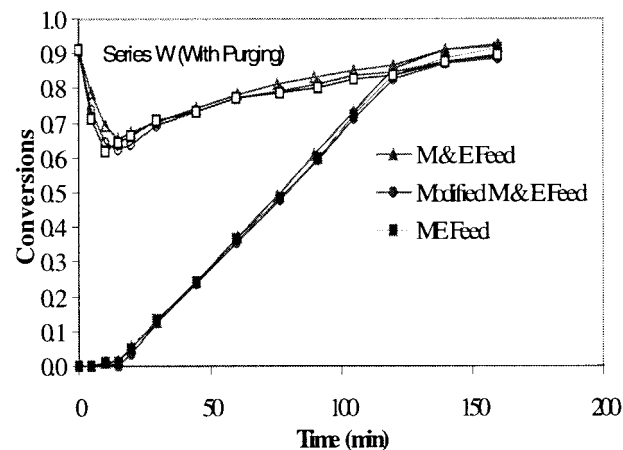
the seed particles and the monomer concentration in the polymer particles.

Figure 3 shows the time evolution of conversions for runs W1, W2-a, and W2-b. The *instantaneous conversion* was defined on the basis of the amount of monomer fed into the reactor up to a given time, the polymer in the seed being taken into account. The instantaneous conversion in interval III is equivalent to monomer conversion in the polymer particles, because of negligible solubility of styrene in the water phase. The initial value of instantaneous conversion is 0.91 because the reactor was initially loaded with seed particles containing the monomer by the weight ratio of 1/10. The *overall conversion* is defined as the weight ratio of the polymer formed in the reactor to the total monomer in the recipe. At the end of feeding, both these conversions approach each other (note that they do not coincide because the weight of the seed particles is not considered for calculation of the overall conversion). No appreciable variation in the rate of the reaction was observed for all runs. An inhibition period in the range of 10–15 min was observed for all experiments. During this period, the monomer was accumulated in the reactor, resulting in a decreasing polymer/monomer weight ratio in the polymer particles with time. The instantaneous conversion (polymer weight ratio in the polymer particles) was reduced to a value around 0.60 where the partially monomer-swollen micelles were still able to adsorb radicals and become polymer particles.<sup>14</sup> Once the polymerization reaction started, the monomer conversion in the polymer particles increased with time until the end of the monomer feeding.

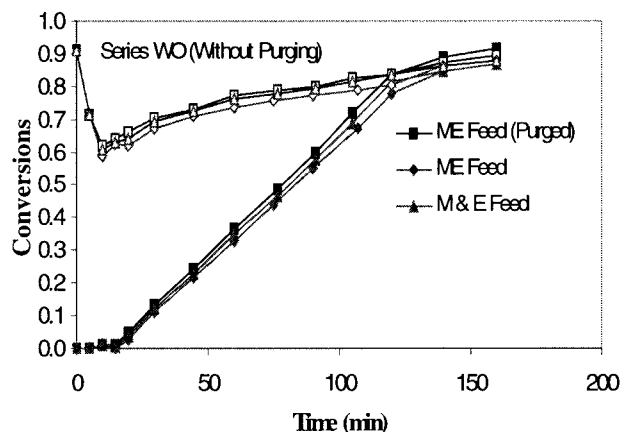
It has been reported in the literature that semibatch emulsion polymerization processes

may have inhibition periods since the monomer emulsion feed is continuously added to the reactor.<sup>6,7</sup> The semibatch emulsion polymerization processes with the monomer emulsion feed are more prone to inhibition effects, compared with the semibatch processes with neat monomer feed. This is caused by incoming water containing dissolved oxygen, which acts as an inhibitor to the reaction. If the monomer emulsion feed is not continuously purged with nitrogen, the water contamination with oxygen may have an inhibition effect on the rate of polymerization.

Figure 4 compares the conversion–time data of the experiments of series WO, which were carried out with no purging during feeding. The rate of polymerization during the initial period of feeding is almost identical for all cases, but a difference develops as the feeding continued. The rate of polymerization for the run with two streams and without N<sub>2</sub> purging, WO2, is only slightly lower than are those from series W that used a nitrogen blanket over the feed, whereas the rate of polymerization for the run with a single-stream monomer emulsion feed and without N<sub>2</sub> purging, WO1, is noticeably lower than are those of series W and run WO2. This indicates that when a monomer emulsion is used as the feed, the inhibition effect is more pronounced if purging is not carried out. This is perhaps because of the foaming of monomer emulsions due to rigorous stirring, which gradually sucks the air into the feed. Such an effect was less if two separate streams of feeds



**Figure 3** Time evolution of (filled symbols) overall conversion and (empty symbols) instantaneous conversion for semibatch emulsion polymerizations using single-stream ME feed (W1), double-stream M & E feed (W2-a), and modified double-stream M & E feed (W2-b). All feedings were performed under nitrogen purging.



**Figure 4** Time evolution of (filled symbols) overall conversion and (empty symbols) instantaneous conversion for semibatch emulsion polymerizations using single-stream ME feed (WO1) and double-stream M & E feed (WO2) in the absence of nitrogen purging. The results are compared with those from the single-stream ME feed run (W1), which was carried out with nitrogen purging.

were used. The extent of the inhibition effect might be more appreciable at a higher monomer feed rate, at which the rate of polymerization is less tightly controlled by the rate of monomer addition. The size data given in Table II indicate that, for all runs, the number of particles was also constant (the number of particles equals to the volume of the polymer phase at the end of reaction, which is almost constant for all runs, divided by the average volume of particles. The latter is easily calculated using the size data given in Table II).

## CONCLUSIONS

We conclude, in the context of this study, that a single-stream monomer emulsion feed, generally applied in industry, is equivalent to a double-

stream feed of a monomer and an aqueous solution of an emulsifier if nitrogen purging is employed. In the absence of nitrogen, a lower rate of polymerization is obtained for the single-stream feed, compared to the double-stream feed, due to the inhibition effect. No appreciable variation in the number of polymer particles was obtained by using the two feeds. It can be concluded that the incoming monomer-swollen micelles were disintegrated to supply emulsifier molecules for the stability of growing particles, before they can capture radicals and become polymer particles.

## REFERENCES

1. Naidus, H. *Ind Eng Chem* 1953, 45, 712.
2. Krackler, J. J.; Naidus, H. *J Polym Sci Part C* 1969, 27, 207.
3. Gerrens, H. *J Polym Sci Part C* 1969, 27, 77.
4. Masa, J. A.; Forcada, J.; Asua, M. *Polymer* 1993, 34, 2853.
5. Sajjadi, S.; Brooks B. W. *J Appl Polym Sci* 1999, 74, 3094.
6. Sajjadi, S.; Brooks B. W. *J Appl Polym. Sci* 2001, 79, 582.
7. Sajjadi, S.; Brooks B. W. *J Polym Sci Polym Chem Ed* 2000, 38, 528.
8. Vanderzande, A. G.; Rudin, A. In *ACS Symposium Series 492*; Daniels, E. S.; Sudol, E. D.; El-Aasser, M. S., Eds.; American Chemical Society: Washington, DC, 1992; p 114.
9. Hong, P. O.; Lee, J. M. *Ind Eng Chem Process Des Dev* 1985, 22, 130.
10. Tang, P. L.; Sudol, E. D.; Adams, M.; El-Aasser, M. S.; Asua, J. M. *J Appl Polym Sci* 1991, 42, 2019.
11. Aniasson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondra, C. *J Phys Chem* 1976, 80, 905.
12. Brooks, B. W. *Brit Polym J* 1973, 5, 199.
13. Liotta, V.; Georgakis, C.; Sudol, E. D.; El-Aasser, M. S. *Ind Eng Chem Res* 1997, 36, 3252.
14. Sajjadi, S. *J Polym Sci Polym Chem Ed*, submitted for publication.