

Seeded Emulsion Polymerization of *n*-Butyl Acrylate Utilizing Miniemulsions

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SYNOPSIS

Nucleation of polymer particles in the seeded emulsion polymerization of *n*-butyl acrylate (BuA) was studied through experiments designed to control the amount of new particles formed. The results show that for the batch and semicontinuous seeded polymerization of BuA, a small amount of new particles was formed in the system in which the monomer was added neat, whereas a significant amount of new particles was formed when the monomer was added as a miniemulsion. This suggests that new particles formed in the miniemulsion process were from nucleation of the monomer droplets. These experiments also showed that monomer-droplet nucleation decreased with increasing seed concentration in the reactor. For the seeded semicontinuous polymerizations, monomer-droplet nucleation decreases with decreasing BuA miniemulsion feed rate. The results also show that monomer-droplet nucleation takes place whenever miniemulsion droplets exist in the reactor. This study suggests that miniemulsions can be used to control the particle size distribution of a polymer latex system.

INTRODUCTION

Monomer droplets are not considered to play a significant role as sites of particle nucleation in conventional emulsion polymerizations, instead acting as monomer reservoirs. However, monomer droplets have been postulated to be the main locus of particle nucleation in miniemulsion polymerizations. In 1973, Ugelstad, El-Aasser, and Vanderhoff¹ reported results on the emulsion polymerization of styrene in a system prepared using a mixed emulsifier system of sodium dodecyl sulfate and hexadecanol. They showed by optical and transmission electron microscopy that the initial sizes of the emulsion droplets, ranging from 100 to 400 nm, were similar to those of the final latex particles. Therefore, it was postulated that monomer droplets could be the principal locus for particle nucleation in these polymerizations, which were subsequently referred to as miniemulsion polymerizations.

Since the initial work¹ was published, many investigators have studied miniemulsion polymerizations.²⁻¹⁰ They have also found much indirect evidence for monomer-droplet nucleation. Ugelstad et al.² studied batch miniemulsion copolymerizations of styrene, *n*-butyl acrylate, and methacrylic acid monomer mixtures. They varied the homogenization pressure to obtain different initial monomer droplet sizes and found that the final latex particle size decreased with increasing homogenization pressure. This suggested that initiation had taken place in the monomer droplets. Rodriguez¹⁰ also found similar results for the batch miniemulsion copolymerization of styrene and methyl methacrylate by varying the duration of sonification or the hexadecane concentration to vary the initial droplet sizes. He found that the final latex particle size decreased and the polymerization rate increased with decreasing initial monomer droplet size. Other investigators have also found indirect evidence for monomer-droplet nucleation.^{2-4,6-9}

The objective of this work is to further the understanding of initiation in miniemulsion polymerization by comparing seeded polymerizations of BuA in which the monomer is added as a conventional

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emulsion and as a miniemulsion. The variables of interest are the concentrations of seed and monomer in the reactor, which are used to control new particle formation.

EXPERIMENTAL

Materials

Sodium hexadecyl sulfate (SHS) was prepared by reacting hexadecanol with chlorosulfonic acid with subsequent neutralization of the alkyl sulfonic acid with sodium hydroxide in isobutanol.¹¹ The salt form (SHS) was recrystallized first from an isobutanol/water mixture and then from pure isobutanol. The product was extracted with diethyl ether for 3 days before drying under vacuum.

n-Butyl acrylate (Aldrich) was distilled under reduced pressure (50 mm Hg) of dry nitrogen. The purified monomer was stored at -2°C . Hexadecane (Aldrich), sodium bicarbonate (Fisher), ammonium persulfate (FMC), hydroquinone (Fisher), and phosphotungstic acid (Fisher) were used as received. The water was distilled and deionized (DDI).

The Polymerization Process

The polymerization recipes are given in Table I. The poly(*n*-butyl acrylate) (PBuA) seed was prepared

Table I Recipes for the Seeded Polymerization of *n*-Butyl Acrylate

Ingredients	Quantity	Quantity
	(g), Series 1	(g), Series 2
<i>Seed Mixture</i>		
PBuA seed	21	6.3
DDI water	101.56	41.34
Sodium hexadecyl sulfate	0.1921	0
Sodium bicarbonate	0.1289	0.1289
<i>Feed Mixture</i>		
BuA	42	56.7
DDI water	77.44	147.66
Sodium hexadecyl sulfate	0.1334	0.3255
Hexadecane (for miniemulsion)	0 or 0.35	0 or 0.86
<i>Initiator Solution</i>		
DDI water	10	10
Ammonium persulfate	0.1289	0.1289

using the method of Maxwell et al.¹² This involved heating *n*-butyl acrylate (375 g), Aerosol MA (5.36 g), sodium bicarbonate (1.27 g), and water (1000 g) to 75°C under a nitrogen atmosphere, with mechanical agitation until emulsification was effected; potassium persulfate (1.24 g) was dissolved in water (104 g), heated to 75°C , and added to the emulsion in the reactor. Polymerization was allowed to continue at 75°C for about 15 h. The seed latex was dialyzed for 4 days, with frequent changes of water to remove excess surfactant. The particle size distribution of the PBuA seed was determined by transmission electron microscopy. The volume average diameter of the PBuA seed latex was found to be 160 nm with a coefficient of variation of 7%.

The miniemulsions were made by first preparing two solutions, sodium hexadecyl sulfate and sodium bicarbonate in DDI water and hexadecane in monomer. These were mixed together for 10 min and then sonified for 60 s (50% duty cycle and power level 7) using a Sonifier Disruptor W-350 (Branson Sonic Power Co.).

Polymerizations were carried out in a glass reactor equipped with a reflux condenser, a stainless steel stirrer, and a nitrogen inlet and sampling tube, and a feed inlet tube connected to a metering pump.

The conditions of all experiments are described in Table II. These are classified into two series according to the seed/monomer weight ratio in the recipe. The first series had a seed/monomer ratio of 1 : 2 (see Table I), whereas the second series had a ratio of 1 : 9. In each series, comparisons were made between the miniemulsion polymerization case and the conventional emulsion polymerization case for the different modes of monomer addition to the reactor, varying from batch conditions to slow feed semicontinuous conditions. Precautions were taken to insure that monomer and emulsifier concentrations in the reactor were the same in both polymerization processes. This was accomplished by controlling feed rates of both the monomer and an aqueous solution of emulsifier in the conventional process to match that of the miniemulsion process.

In run BMAC1/2 (series 1), the seed mixture (see Table I) was heated to 60°C in the reactor, and then the initiator solution was added. After 10 min all of the conventional emulsion was added to start the reaction. The conditions of run BMIN1/2 were similar to run BMAC1/2, except that the monomer was added in the form of a miniemulsion. In runs FNEAT1/2, FMIN1/2, and SMIN1/2, the seed mixture was heated to 60°C in the reactor, and then the initiator solution was added. After 10 min, the monomer mixture was fed semicontinuously to the

Table II Conditions of Seeded Polymerizations of *n*-Butyl Acrylate

Run	Description
BASEED	Poly(<i>n</i> -butyl acrylate) seed
BMAC1/2	Batch conventional emulsion, Series 1 (seed : monomer ratio of 1 : 2)
BMIN1/2	Batch miniemulsion, Series 1
FNEAT1/2	Semicontinuous addition of BuA at 0.3 cc/min, and aqueous solution of surfactant at 0.5 cc/min, Series 1
FMIN1/2	Semicontinuous addition of BuA miniemulsion at 0.8 cc/min (0.3 cc/min based on monomer), Series 1
SMIN1/2	Semicontinuous addition of BuA miniemulsion at 0.4 cc/min (0.15 cc/min based on monomer), Series 1
BMAC1/9	Batch conventional emulsion, Series 2 (seed : monomer ratio of 1 : 9)
BMIN1/9	Batch miniemulsion, Series 2
FMIN1/9	Semicontinuous addition of BuA miniemulsion at 1.564 cc/min (0.5 cc/min based on monomer), Series 2
SMIN1/9	Semicontinuous addition of BuA miniemulsion at 0.782 cc/min (0.25 cc/min based on monomer), Series 2

reactor. For run FNEAT1/2, neat BuA was added at 0.3 cc/min and an aqueous solution of sodium hexadecyl sulfate at 0.5 cc/min; for run FMIN1/2, the feed was added in the form of a miniemulsion at 0.8 cc/min (0.3 cc/min based on BuA), while for run SMIN1/2, the feed was introduced as a mini-

emulsion at 0.4 cc/min (0.15 cc/min based on BuA).

In run BMAC1/9 (series 2), the monomer mixture was heated to 60°C in the reactor, and then the seed mixture (at 60°C) and the initiator solution were added to the reactor to start the reaction. In doing this, the reaction was started at 60°C to minimize the swelling of polymer by monomer before polymerization. Run BMIN1/9 was carried out similarly to run BMAC1/9, except that the monomer was charged into the reactor in the form of a miniemulsion. In run FMIN1/9, the seed mixture was heated to 60°C, then the initiator solution was added, and after 10 min the BuA miniemulsion was added semicontinuously at 1.564 cc/min (0.5 cc/min based on BuA). Run SMIN1/9 was carried out similarly to run FMIN1/9, except that a feed rate of 0.782 cc/min (0.15 cc/min based on BuA) was used.

Samples were withdrawn during the reaction, and the polymerization was short-stopped with a solution of 1% hydroquinone in water. The conversions were determined by drying a known amount of sample in an oven. The particle size distribution of the final latex was determined by transmission electron microscopy, and the results are shown in Table III. For samples from runs FMIN1/2, SMIN1/2, and BMIN1/9, about 1500 particles from three different grids were counted; for the remaining samples, about 500 particles were counted.

The overall conversion is defined as the weight ratio of polymer in the reactor to the total polymer and monomer in the recipe. The instantaneous conversion is the weight ratio of the polymer in the reactor to the total polymer and monomer in the reactor at time *t*.

Table III Final Latex Particle Size Statistics for the Seeded Polymerizations of *n*-Butyl Acrylate

Run	D_v (nm) ^a	D_w (nm) ^b	D_n (nm) ^c	D_w/D_n	S_n^d/D_n
BASEED	160	162	160	1.01	0.07
BMAC1/2	235	248	227	1.09	0.19
BMIN1/2	200	216	190	1.13	0.23
FNEAT1/2	249	258	244	1.06	0.15
FMIN1/2	234	280	198	1.41	0.46
SMIN1/2	234	273	206	1.32	0.40
BMAC1/9	348	357	342	1.04	0.14
BMIN1/9	227	255	214	1.19	0.26
FMIN1/9	212	299	168	1.77	0.53
SMIN1/9	258	296	228	1.30	0.40

^a D_v is the volume average diameter.
^b D_w is the weight average diameter.
^c D_n is the number average diameter.
^d S_n is the standard deviation.

Table IV The Number of Seed Particles, Final Latex Particles, and New Particles Estimated for the Seeded Polymerizations of BuA

Run	D_v (nm)	N_s ($10^{12}/\text{cc}$) ^a	$N_{f,nc}$ ($10^{12}/\text{cc}$) ^b	N_n ($10^{12}/\text{cc}$)	N_n/N_s
BMAC1/2	235	42	48	6	0.14
BMIN1/2	200	43	70	27	0.63
FNEAT1/2	249	36	39	3	0.08
FMIN1/2	234	36	50	14	0.39
SMIN1/2	234	35	47	12	0.34
BMAC1/9	348	13	14	1	0.08
BMIN1/9	227	13	47	34	2.6
FMIN1/9	212	10	50	40	4.0
SMIN1/9	258	10	26	16	1.6

^a N_s is the number of seed particles per cc of final latex.

^b $N_{f,nc}$ is the number of final particles per cc of final latex if no coagulation occurred.

^c N_n is the number of new particles per cc of final latex.

RESULTS AND DISCUSSION

As a result of the particle size analyses, a limited coagulation was found to occur during polymerization in many experiments; a coagulation that resulted in particles with the sizes of doublets, triplets, etc. Therefore, calculations were performed to estimate the number of new particles formed in a polymerization assuming that no coagulation had occurred (see the Appendix). The results of the estimations for all runs are presented in Table IV.

Seeded Batch Polymerization of *n*-Butyl Acrylate

In the seeded batch polymerization cases (BMIN1/2 and BMIN1/9) where the monomer was added

as a miniemulsion, a large number of new particles was produced. For the high seed concentration series (series 1, seed/monomer ratio of 1 : 2), the particle size distributions differ considerably for the two monomer addition conditions as seen in Figure 1 and 2. The particle size distribution for the conventional emulsion process (run BMAC1/2) is narrower than the miniemulsion process and the corresponding final number of latex particles is only slightly greater than the number of seed particles. These results indicate that only a small amount of new particles was formed in the conventional process. However, significant amounts of new particles were formed in the miniemulsion process (run BMIN1/2). The particle size distribution is broader than that of the conventional emulsion process (run

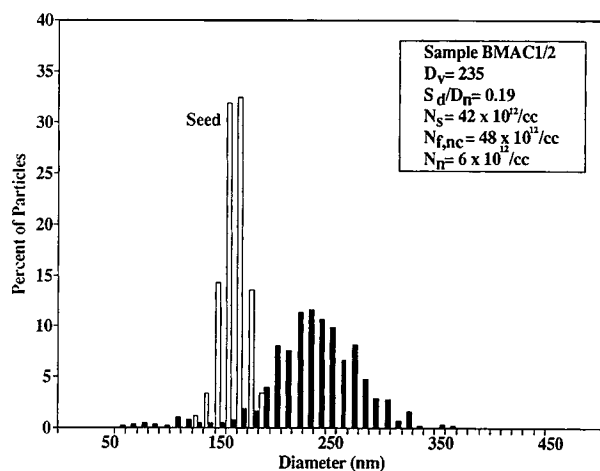


Figure 1 Particle size distribution for run BMAC1/2; batch conventional emulsion polymerization; series 1, seed/monomer ratio of 1 : 2.

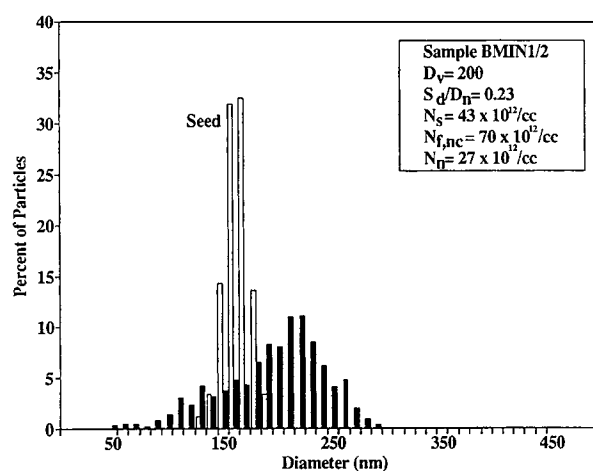


Figure 2 Particle size distribution for run BMIN1/2; batch miniemulsion polymerization; series 1, seed : monomer ratio of 1 : 2.

BMAC1/2), and the final number of particles is almost twice that of the seed. If most of the new particles were formed in the miniemulsion process by homogeneous or micellar nucleation, then a large number of new particles should also be formed in the conventional emulsion process, because the only difference between the two processes is that the miniemulsion process has smaller monomer droplets. These findings suggest that most of the new particles found in the miniemulsion process were formed from the initiation of monomer droplets.

The generation of new particles in the miniemulsion process (run BMIN1/2) was expected to have a significant influence on the reaction kinetics, but this was not the case as seen in Figure 3. The total conversion versus time curves are similar for the miniemulsion and conventional emulsion processes and thus, the reaction rates are approximately the same. This result can be explained by examining the parameters affecting the rate of polymerization in

$$\frac{dx}{dt} = \frac{k_p[M]_p \bar{n} N_p}{M_0 N_A} \quad (1)$$

where k_p is the propagation constant, $[M]_p$ the concentration of monomer in the particles, \bar{n} the number of radicals per particle, N_p the number of particles, M_0 the initial concentration of monomer, and N_A the Avogadro's number. For the polymerization rates to be the same in the two experiments, the product $[M]_p \bar{n} N_p$ must be the same at any time. During the course of the polymerization, however, all three of these may be changing. Despite this, we

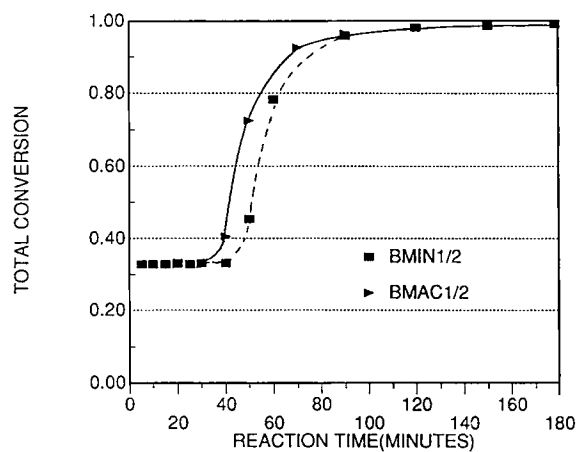


Figure 3 Total conversion versus time curves for series 1; run BMIN1/2, batch miniemulsion polymerization of BuA; and run BMAC1/2, batch conventional emulsion polymerization of BuA.

can make some rough approximations to gain some additional understanding. To calculate \bar{n} at any given conversion, say 60%, we first assume that the monomer concentration in the particles is simply determined by the conversion in Interval III (i.e., all monomer is present in the particles). This assumption should be valid for the case where the monomer was added neat but not necessarily so for the miniemulsion case where monomer droplets are expected to be present. Delgado et al.⁹ showed through thermodynamic analysis that the fraction of monomer existing in the form of droplets was below 0.1 at 60% conversion in a VAc-BuA miniemulsion copolymerization system. A similar behavior is expected for the BuA homopolymerization system and thus $[M]_p$ should not be off by more than 10%. The second assumption is that the number of particles is the same as that determined at the end of the polymerization. However, both polymerizations show evidence of small particles (see Figs. 1 and 2), which implies that particles are nucleated throughout much of the polymerization. Therefore, the value of \bar{n} will be underestimated. This is not of any consequence in this analysis, as will be shown.

Based on the above assumptions, \bar{n} was calculated at 60% conversion to be 23 for BMAC1/2 and 15 for BMIN1/2. These values are within the region termed Smith-Ewart Case 3 ($\bar{n} \gg 1$). This region has been postulated to have polymerization kinetics which are independent of particle number.¹³ This stems from the following reasoning. For high \bar{n} the pseudo-bulk equation should apply:¹⁴

$$\bar{n} = N_A \left(\frac{f k_i [I] v_p}{k_t N_p} \right)^{1/2} = \frac{N_A}{N_p} \left(\frac{f k_i [I] V_p}{k_t} \right)^{1/2} \quad (2)$$

where f is the initiator efficiency, k_i the rate constant for initiator decomposition, $[I]$ the initiator concentration, v_p the molar volume of particles, V_p the total particle volume and k_t the termination constant. When substituted into eq. (1), eq. (2) becomes

$$\frac{dx}{dt} = \frac{k_p [M]_p}{M_0} \left(\frac{f k_i [I] V_p}{k_t} \right)^{1/2} \quad (3)$$

Although this expression resembles that for bulk polymerization, the term $(f k_i [I])$ actually represents the radical adsorption rate. Attempts at modeling the latter have been made based on various theories and these generally include some dependency on particle size and number. Thus, polymerization should still show some dependency on these.

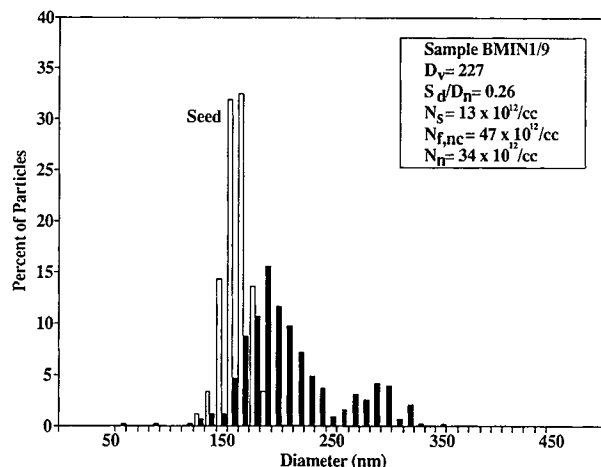


Figure 4 Particle size distribution for run BMIN1/9; batch miniemulsion polymerization; series 2, seed/monomer ratio of 1 : 9.

Nonetheless, the above experimental results are qualitatively understandable based on Case 3 kinetics.

Monomer-droplet nucleation produced a larger number of new particles in the miniemulsion polymerizations using a lower seed concentration (series 2, seed/monomer ratio of 1 : 9) as shown in Figure 4. Again, a small amount of new particles was formed in the conventional emulsion process (Fig. 5). These results indicate that decreasing the seed concentration increases the probability of monomer-droplet nucleation in a miniemulsion polymerization. The number of new particles formed with the low seed

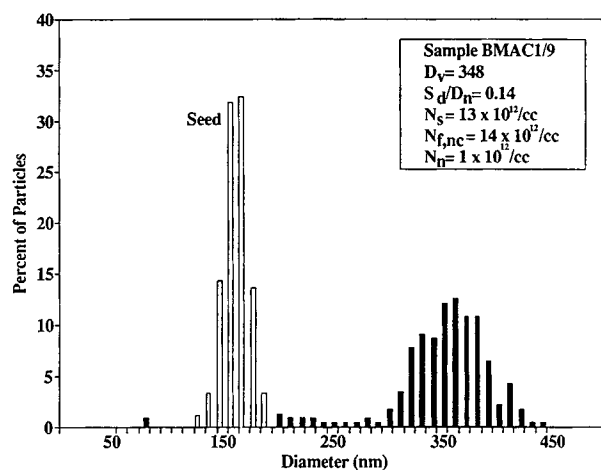


Figure 5 Particle size distribution for run BMAC1/9; batch conventional emulsion polymerization; series 2, seed/monomer ratio of 1 : 9.

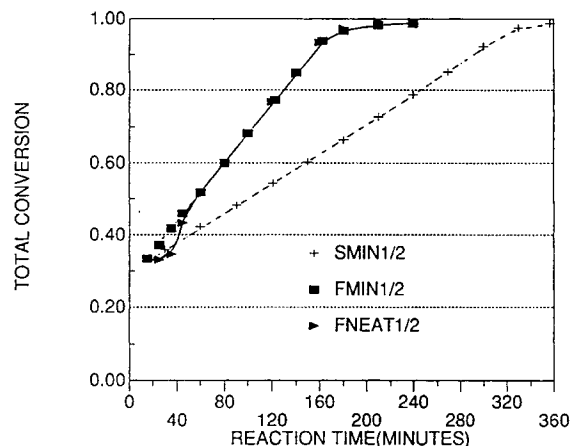


Figure 6 Total conversion versus time curves for series 1; run SMIN1/2 with semicontinuous addition of BuA miniemulsion at 0.15 cc/min of monomer; run FMIN1/2 with semicontinuous addition of BuA miniemulsion at 0.3 cc/min of monomer; and run FNEAT1/2 with semicontinuous addition of neat BuA at 0.3 cc/min.

concentration (Fig. 4) was $34 \times 10^{12}/\text{cc}$, which is a 26% increase over that of the high seed concentration run of $27 \times 10^{12}/\text{cc}$.

Seeded Semicontinuous Polymerization of *n*-Butyl Acrylate

In the seeded semicontinuous polymerizations of *n*-butyl acrylate, the kinetic results indicate that the polymerization rate was controlled by the feed rate. Figure 6 shows the total conversion versus reaction time curves for the semicontinuous polymerizations in series 1, while Figure 7 shows the corresponding instantaneous conversion versus time curves. The transient behavior when the feed is started may be attributed to some inhibition effects as seen previously in the batch studies. The inhibition times are roughly comparable to those in Figure 3. After 40% conversion, the reaction rates are the same for both processes because the kinetics are controlled by the BuA feed rate. Note that the polymerization rate of FMIN1/2 is twice that of SMIN1/2, which had a monomer feed rate of 0.15 cc/min.

Although the kinetics of these reactions are controlled by the BuA feed rate, their particle size distributions are very different. The PSDs given in Figures 8, 9, and 10 indicate that monomer-droplet nucleation produced a large number of new particles in the seeded semicontinuous miniemulsion polymerizations, while only a relatively small amount of new particles was formed in run FNEAT1/2 where

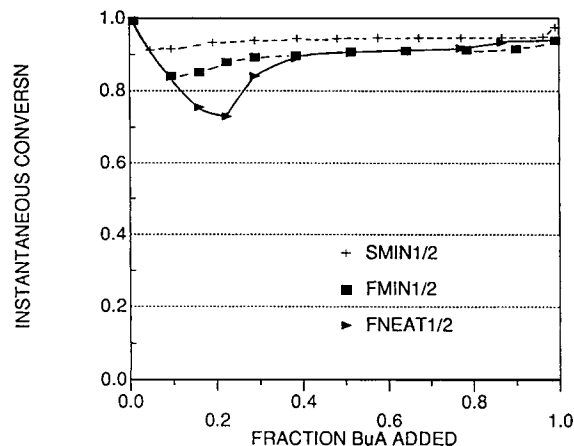


Figure 7 Fraction BuA added versus instantaneous BuA conversion for series 1; run SMIN1/2 with semicontinuous addition of BuA miniemulsion at 0.15 cc/min of monomer; run FMIN1/2 with semicontinuous addition of BuA miniemulsion at 0.3 cc/min of monomer; and run FNEAT1/2 with semicontinuous addition of neat BuA at 0.3 cc/min.

the feed was introduced as neat BuA and an aqueous solution of surfactant. Comparing Figures 8 and 9, the number of new particles formed in the miniemulsion process is almost five times that of the neat process.

The particle size distributions show that in the case where the seed/monomer weight ratio was 1 : 2, decreasing the miniemulsion feed rate by half, only slightly decreases the number of new particles initiated in miniemulsion droplets. This phenom-

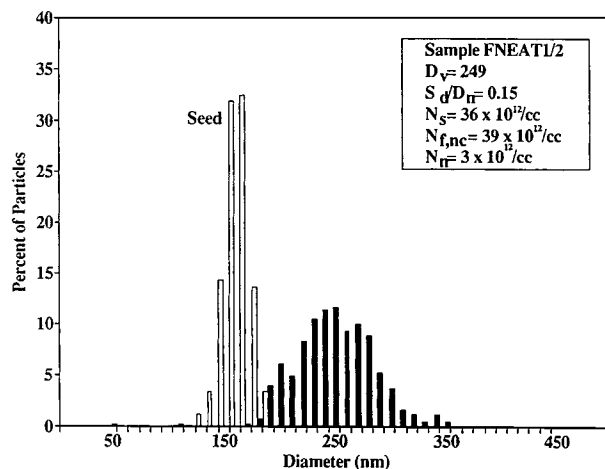


Figure 8 Particle size distribution for run FNEAT1/2; semicontinuous addition of neat BuA at 0.3 cc/min, and aqueous solution of surfactant at 0.5 cc/min; series 1, seed/monomer ratio of 1 : 2.

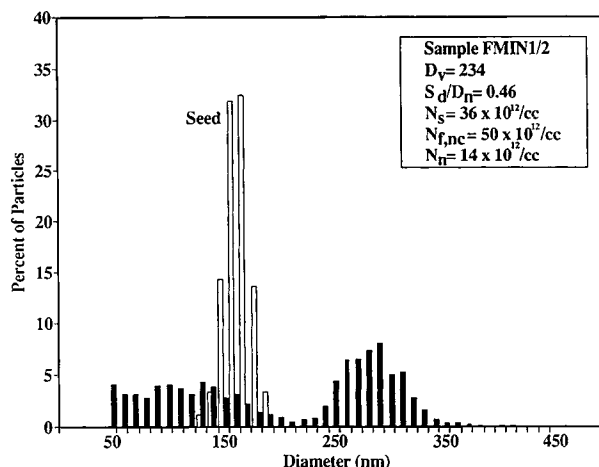


Figure 9 Particle size distribution for run FMIN1/2, semicontinuous addition of BuA miniemulsion, 0.3 cc/min of monomer; series 1, seed/monomer ratio of 1 : 2.

non is greatly enhanced in the results obtained in the low seed concentration series (Figs. 11 and 12). The number of new particles formed in the polymerization using the faster feed rate (FMIN1/9) is more than twice that of the slower one (SMIN1/9). Figures 11 and 12 also indicate that monomer-droplet nucleation took place whenever miniemulsion droplets were being fed in the system, and the faster feed rate produced a larger population of small particles compared to the slower feed rate.

By comparing all these results, it is clear that not all miniemulsion droplets become polymer particles.

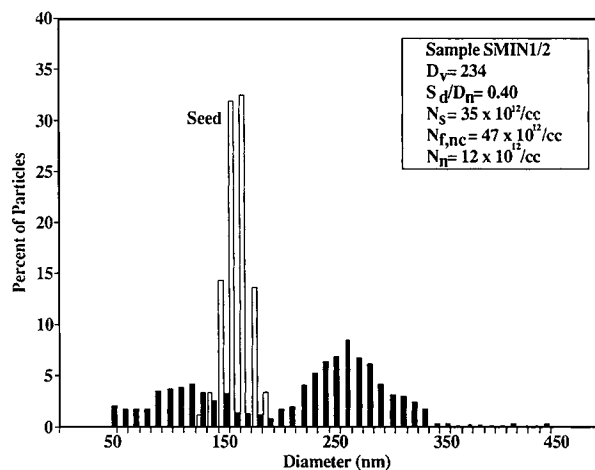


Figure 10 Particle size distribution for run SMIN1/2; semicontinuous addition of BuA miniemulsion, 0.15 cc/min of monomer; series 1, seed/monomer ratio of 1 : 2.

The disappearance of monomer droplets must also occur by another mechanism, such as diffusion to growing particles or by collision with polymer particles as postulated by Rodriguez et al.¹⁵ Some quantitative estimation of the importance of the latter mechanism has been given by Asua et al.¹⁶

SUMMARY

Particle nucleation in miniemulsion polymerization was studied by comparing seeded polymerizations of BuA, in which the monomer was added as a conventional emulsion and a miniemulsion. The variables of interest were the concentrations of seed and the mode of monomer addition. In the seeded batch polymerization of BuA, a small amount of new particles was formed in the system in which the monomer was added neat, whereas a significant amount of new particles was formed when the monomer was added as a miniemulsion. This suggests that new particles formed in the miniemulsion process resulted from nucleation of the monomer droplets. These experiments also showed that monomer-droplet nucleation decreased with increasing seed concentration in the reactor.

The seeded semicontinuous polymerizations of BuA in which the feed stream was a miniemulsion produced a large number of new particles. Monomer-droplet nucleation was found to decrease with increasing seed concentration in the reactor. It was also found that monomer-droplet nucleation decreased with decreasing miniemulsion feed rate. This

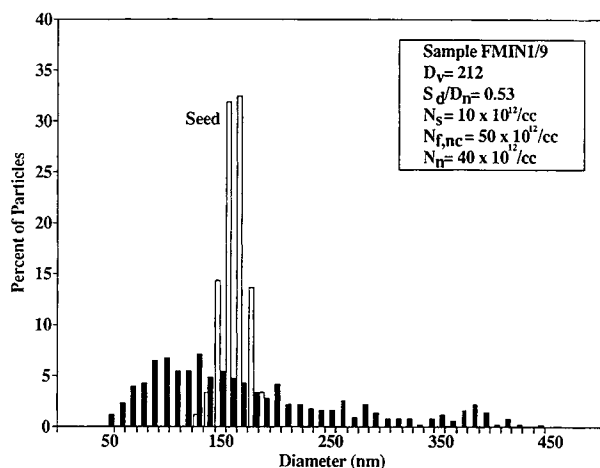


Figure 11 Particle size distribution for run FMINI/9; semicontinuous addition of BuA miniemulsion at 0.5 cc/min of monomer; series 2, seed/monomer ratio of 1 : 9.

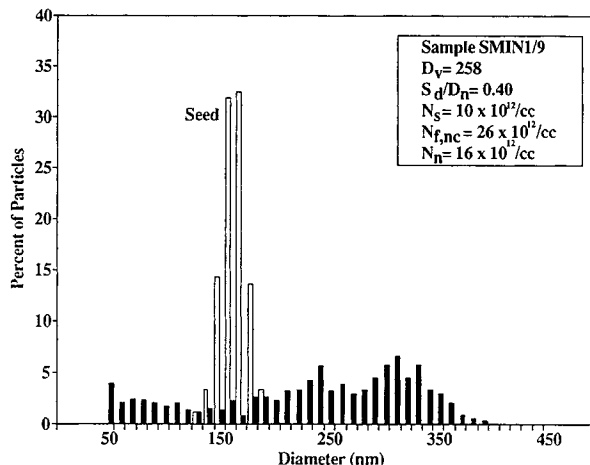


Figure 12 Particle size distribution for run SMINI/9; semicontinuous addition of BuA miniemulsion at 0.25 cc/min of monomer; series 2 seed/monomer ratio of 1 : 9.

study indicated that monomer-droplet nucleation can take place whenever miniemulsion droplets exist in the reactor. The faster the feed rate the larger is the population of small particles produced. The study suggests that miniemulsions can be used to control the particle size distribution of a polymer latex system by adjusting particle numbers, mode of monomer addition, and monomer feed rates.

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APPENDIX

Estimation of the Number of New Particles Formed

The results from run FMIN1/2 will be used as an example of the estimation of the number of new particles formed in a polymerization assuming that no coagulation had occurred. Figure A.1 is the particle size distribution (PSD) determined for the latex produced from run FMIN1/2. The narrow peak is the PSD of the seed, while the other peaks represent the PSD of the final latex. The number of seed particles per cc of final latex (N_s) was calculated from the volume average diameter of the seed, the weight of seed, and the volume of the final latex. The final number of latex particles per cc of final latex (N_f) was calculated from the volume average diameter of the final latex, the weight of final polymer and the volume of the final latex.

Figure A.1 indicates that a significant amount of new particles was formed in run FMIN1/2, but the final number of latex particles was similar to that

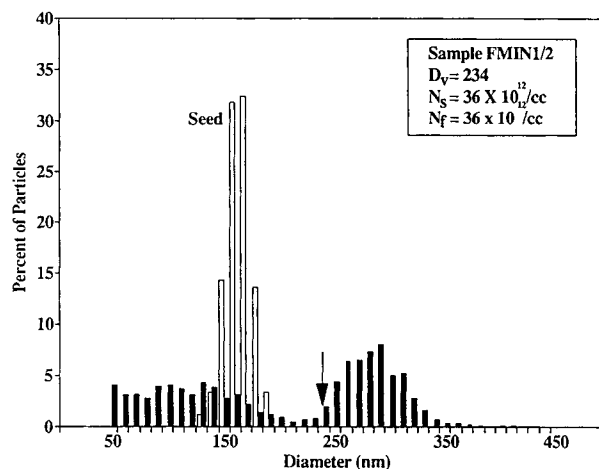


Figure A.1 Particle size distribution for run FMIN1/2; semicontinuous addition of BuA miniemulsion, 0.3 cc/min of monomer; series 1, seed/monomer ratio of 1 : 2. Arrow indicates average size of final particles assuming no coagulation or new particle generation.

of the seed. The arrow on Figure A.1 indicates the theoretical volume average diameter (D_t) of the final latex if all the monomer was uniformly distributed in the seed (i.e., no new particles or coagulation of the seed). This evidence suggests that coagulation occurred during the polymerization process.

The final number of latex particles if no coagulation occurred ($N_{f,nc}$) was estimated by assuming that:

1. The population of particles which have diameters (D_L) larger than the theoretical diameter (D_t) were involved in coagulation.
2. A negligible amount of new particles having diameters larger than D_t resulted from monomer-droplet nucleation.

Estimation of the number of new particles was carried out as follows:

- From the total number of particles counted from the TEM micrographs (N_T), the number of large particles (N_L) larger than D_t and the number of small particles ($N_T - N_L$), which were not involved in coagulation, can be found.
- With N_L and their diameter D_L , the total volume of large particles (V_L) was determined.
- From V_L and D_t the number of large particles

if no coagulation occurred ($N_{L,nc}$) was calculated.

- $N_{L,nc}$ was then added to the number of small particles ($N_T - N_L$) to determine the total number of particles which should be counted from TEM micrographs if no coagulation occurred ($N_{T,nc}$).
- The number of final latex particles if no coagulation occurred ($N_{f,nc}$) was adjusted by the ratio $N_{T,nc}/N_T : N_{f,nc} = N_f(N_{T,nc}/N_T)$. The number of new particles (N_n) was found by subtracting the seed particles (N_s) from the final number of particles if no coagulation occurred.

Example of Estimation for Run FMIN1/2

- $D_t = 234$ nm
- $N_f = 36 \times 10^{12}/\text{cc}$
- $N_T = 1626$
- $N_L = 823$
- $V_L = 9.9 \times 10^9$ nm³
- $N_{L,nc} = V_L/(\pi D_t^3/6) = 1475$
- $N_{T,nc} = 1475 + (1626 - 823) = 2278$
- $N_{f,nc} = 36 \times 10^{12}/\text{cc} (2278/1626) = 50 \times 10^{12}/\text{cc}$
- $N_n = 50 \times 10^{12}/\text{cc} - 36 \times 10^{12}/\text{cc} = 14 \times 10^{12}/\text{cc}$