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SEMIBATCH SEEDED EMULSION POLYMERIZATION OF ACRYLIC MONOMERS: BIMODAL PARTICLE SIZE DISTRIBUTION

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ABSTRACT

Injecting sodium dodecyl sulfate (SDS) into the reaction medium induces a second crop of tiny primary particles (i.e., secondary nucleation) in semibatch seeded emulsion polymerization. Secondary nucleation may thus result in latex products with a bimodal particle size distribution (BPSD-Latices). The concentration of seed particles ([Seed]) is the most important variable for controlling the particle-size-distribution-related parameter (P), followed by the time when the surfactant is injected into the reactor (t_s). The resultant latex particle size (d_p) is not sensitive to changes in the concentration of injected SDS ([SDS]). Parameter P decreases with increasing [Seed] or t_s . This implies retarded secondary nucleation during monomer addition when [Seed] or t_s increases. An experiment with smaller values of [Seed] and t_s favors formation of BPSD-Latices. The data clearly show a bimodal particle size distribution when P is greater than approximate 70%. Parameter P correlates well with the total seed particle surface area (A_s) regardless of the seed particle size, and P (%) is proportional to A_s (cm²) to the -0.319 power. Thus, A_s is a very useful parameter for manipulation of the resultant latex particle size and particle size distribution.

INTRODUCTION

Emulsion polymerization [1] involves dispersion of water-insoluble monomer in the surfactant solution, followed by addition of a persulfate initiator to start the reaction. Semibatch emulsion polymerization [2] is widely used to manufacture latex products due to its efficient heat transfer and operational flexibility in making various products with controlled particle composition and morphology. A latex product comprises innumerable submicron polymer particles (ca. 50–1000 nm in diameter) dispersed in water. The latex particles are thermodynamically unstable, and these particles can be stabilized by anionic/nonionic surfactants which provide electrostatic/steric stabilization actions against the attractive van der Waals force among interactive particles. Latex particles are generated by either micellar [3, 4] or homogeneous [5, 6] nucleation mechanisms. Latex products are widely used in applications such as coatings, adhesives, thermoplastics, and synthetic rubbers.

Latex products with a bimodal particle size distribution (abbreviated as BPSD-Latices) show a minimum viscosity when the volume fraction of small particles is in the 0.25–0.30 range [7–9]. The point at which minimum viscosity is achieved for BPSD-Latices corresponds to the best particle packing efficiency. This is achieved by packing large particles randomly and filling the voids with small particles to obtain a minimum void volume. This condition is essential for producing concentrated polymer dispersions, which is highly desirable in industry. BPSD-Latices are produced by blending two monodisperse polymer dispersions with sufficiently different sizes. Another approach is to generate a second crop of small particles in situ by injecting surfactant into the reaction medium (i.e., secondary nucleation) during semibatch emulsion polymerization. Such a technique has been demonstrated in our previous work [10, 11], but the experimental data are rather limited.

The objective of this work was therefore to systematically study how to control the latex particle size and particle size distribution in semibatch emulsion polymerization. The emulsion polymer chosen for this study comprises 95% butyl methacrylate and 5% methacrylic acid (a typical coating composition). A seeded technique (i.e., number of latex particles in the reaction system is known immediately before monomer feeding starts) was used to gain a better understanding of secondary nucleation during monomer addition. This is because development of BPSD-Latices is the subject of major interest, and nucleation of primary particles during the very early stage of polymerization is beyond the scope of this study.

EXPERIMENTAL

Materials

The chemicals used were butyl methacrylate (BMA) (Mitsubishi Rayon Co.), methacrylic acid (MAA) (Mitsubishi Rayon Co.), sodium dodecyl sulfate (SDS) (Henkel Co.), nonyl phenol-40 moles ethylene oxide adduct (NP-40) (Union Carbide), sodium persulfate (Riedel-de Haen), sodium bicarbonate (Riedel-de Haen), nitrogen (Ching-Feng-Harng Co.), and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance $< 0.057 \mu\text{S}/\text{cm}$). The monomers BMA and MAA were distilled under reduced pressure before use. All other chemicals were used as received.

Polymerization Process

Semibatch emulsion polymerization was carried out in a 1-L glass reactor equipped with a 4-bladed agitator, a thermometer, and a condenser. A typical recipe is shown in Table 1. All process water along with seed particles and sodium bicarbonate were charged into the reactor at room temperature. The initial reactor charge was purged with nitrogen for 10 minutes to remove dissolved oxygen while the reactor temperature was brought to 80°C, followed by addition of the initiator solution. Subsequently, the monomer mixture was fed into the reactor over 240 minutes by an FMI pump (monomer feed rate = 0.79 g/min). The surfactant solution was injected into the reactor 5 minutes after the start of monomer feed to induce a second crop of small particles. The polymerization temperature was kept at 80°C throughout the reaction. After monomer feeding was complete, the reaction system was maintained at 80°C for 60 minutes to reduce the level of residual monomer. The theoretical solid content at the end of polymerization is 50%. The recipe used for preparing the seed latex includes 1) initial reactor charge: 990.20 g H₂O, 0.71 g NaHCO₃, 0.12 g SDS, 0.24 g NP-40, 44.86 g BMA, and 2.36 g MAA; 2) monomer emulsion feed: 106.20 g H₂O, 1.06 g SDS, 2.12 g NP-40, 403.72 g BMA, and 21.24 g MAA; and 3) initiator solution: 23.60 g H₂O and 1.89 g Na₂S₂O₈. The monomer emulsion feed rate is 2.21 g/min, and the theoretical solid content is 30%. The seed latex was prepared in a similar manner except that monomer emulsion feeding was started 15 minutes after addition of the initiator solution to allow

TABLE 1. A Typical Recipe for the Semibatch Seeded Emulsion Polymerization of Butyl Methacrylate/Methacrylic Acid (95/5)

	Chemicals	Weight, g
Initial reactor charge	H ₂ O	162.59
	NaHCO ₃	0.30
	Seed latex (29.6% solid content) ^a	13.05
Monomer feed	BMA	180.05
	MAA	9.48
Initiator solution	H ₂ O	10.00
	Na ₂ S ₂ O ₈	0.80
Surfactant charge	H ₂ O	17.41
	SDS ^b	5.80
Total weight, g		399.48
Total solid content, %		50

^a2% seed latex particles based on total monomer.

^b3% SDS based on total monomer which is added 5 minutes after the start of monomer feed.

the development of particle nuclei. The resultant seed latex has an average particle size of 212 nm based on four batches.

The latex product was then filtered through a 40-mesh (0.42 mm) screen and a 200-mesh (0.074 mm) screen in series to collect the filterable solids. Scraps adhering to the agitator, thermometer, and reactor wall were also collected. Total solid content was determined by the gravimetric method. The average particle size (d_p) data were obtained from the dynamic light-scattering method (Otsuka, Photal LPA-3000/3100). The latex sample was diluted with water to adjust the number of photons counted per second (cps) to 8,000–12,000. The number of accumulation times was set at 50 throughout this work. The d_p data reported in this work represent an average of at least three measurements, and the errors have been estimated to be 7% or less.

RESULTS AND DISCUSSION

Two-Level Factorial Design

First, the concentration of seed particles ([Seed]: 2–10% based on total monomer), the amount of SDS injected during monomer addition ([SDS]: 1–3% based on total monomer), and the time when the SDS solution was injected into the polymerization system (t_s : 5–35 minutes) were chosen as the variables of a two-level factorial design (nine points in a designed cube, one midpoint included) to quantitatively analyze their effects on P , which is related to particle size distribution. The numeric values in the above parentheses represent the lowest level and the highest level in the factorial design. Parameter P represents the weight percentage of fed monomer that does not contribute to the growth of seed particles. It can be calculated by the following equations:

$$P = (d_f'^3 - d_f^3)/d_f'^3 \times 100\% \quad (1)$$

$$d_f' = [1 + W_m/W_s]^{1/3} d_s \quad (2)$$

where d_f is the experimental d_p at the end of polymerization, d_f' is the calculated d_p at the end of polymerization when neither secondary nucleation nor limited flocculation takes place during monomer addition, d_s is the seed particle size, W_s is the weight of seed particles, and W_m is the total weight of fed monomer. During monomer addition, growth of latex particles via polymerization of the imbibed monomer results in an increase in the particle–water interfacial area. The newly created particle surfaces require more surfactant to maintain adequate colloidal stability. Otherwise, limited flocculation [5, 6, 12] may occur during monomer addition to reduce the total particle surface area. Limited flocculation involves growth of latex particles via mild aggregation among themselves. The surface charge density of these particles increases due to the reduced particle–water interfacial area. This may retard further flocculation and, thereby, make the lightly aggregated particles stable again. Limited flocculation is reflected in the increased particle size. During monomer addition, injecting SDS into the reactor may cause formation of a second crop of primary particles. Secondary nucleation reduces the average particle size and broadens the particle size distribution. Moreover, the newly borne particle nuclei create more particle–water interfacial area. The polymerization system may thus need more surfactant for appropriate colloidal stability. The larger the value of P ,

the greater is the probability of generating a second crop of small particles during monomer addition. Parameter P may thus serve as a qualitative indicator for the polydispersity of the final latex particle size distribution.

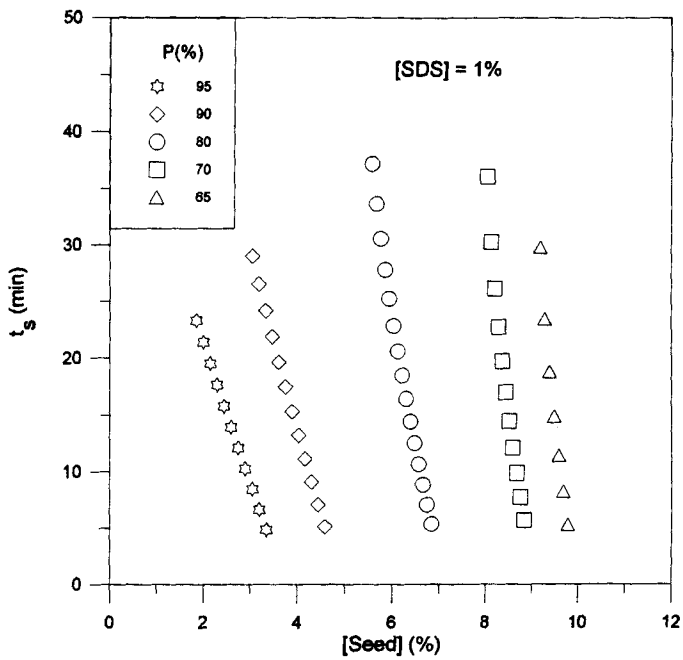
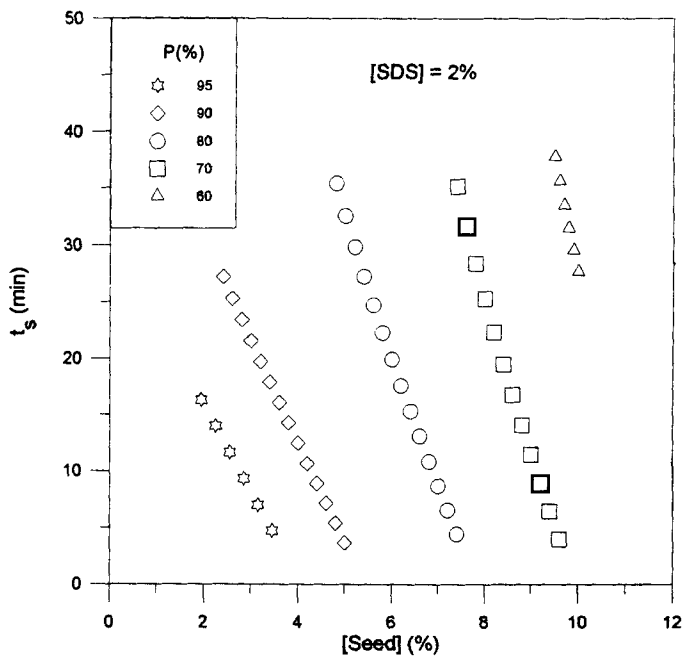
The midpoint experiment was carried out twice to test the batch-to-batch variations in this study. The data of d_p , P , total solid content, and total scrap are 317 ± 7 nm, $80 \pm 1\%$, $45.9 \pm 0.3\%$, and $0.84 \pm 0.06\%$, respectively. The total scrap data represent the large flocs collected by a 40-mesh screen and a 200-mesh screen in series plus those adhering to the agitator, thermometer, and reactor wall. The reproducibility of the midpoint experiment is reasonably good. The positive sign of P implies the generation of a second crop of primary particles during monomer addition. The overall average of the total scrap data is only 0.7%, indicating that the recipe used in the factorial design is quite stable. The experimental data show that [Seed] (-31.27%) is the most important parameter in determining the magnitude of P , followed by t_s (-9.90%) and then [SDS] (-1.14%). The numeric values in the above parentheses represent the standardized effects of variables on P when these variables are changed from the lowest level to the highest level. For example, P will decrease 31.27% with respect to the overall average (78.89%) when [Seed] is changed from the lowest level (2%) to the highest level (10%). Thus, the number of primary particles nucleated during monomer addition is greatly reduced and the particle size distribution becomes narrower when [Seed] increases. The injected surfactant may form micelles for subsequent micellar particle nucleation (if [SDS] > CMC) or simply stabilize the particle nuclei precipitated out of the aqueous phase. It is expected that the higher the level of [SDS], the greater is the probability of inducing secondary nucleation during monomer addition. Surprisingly, the amount of SDS injected into the reaction medium does not play an important role in preparing BPSD-Latices.

Based on this factorial design, the following empirical equations were derived to predict P .

$$\begin{aligned}
 P (\%) = & 79.9691 - 15.6358A - 0.5698B - 4.9498C + 1.1851AB \\
 & + 0.2565AC - 2.2600BC - 0.8966ABC - 2.0863A^2 \\
 & + 0.07600B^2 + 0.6605C^2
 \end{aligned} \quad (3)$$

where $A = 0.25[\text{Seed}] - 1.5$, $B = [\text{SDS}] - 2$, and $C = 0.06667t_s - 1.3333$. Figures 1-3, constructed from Eq. (3), show the contour plots of P when [SDS] is kept at 1, 2, and 3%, respectively. At constant t_s , P decreases rapidly with increasing [Seed] due to the enhanced particle-water interfacial area. The probability that particle nuclei generated during monomer addition are captured by seed particles increases significantly with total particle surface area. Parameter P is not very sensitive to changes in t_s , and the rate of change in t_s with [Seed] decreases (i.e., t_s becomes more important in controlling P) when [SDS] increases from 1 to 3% (see Figs. 1-3). Considering the curve with $P = 80\%$ in Fig. 3, for example, [Seed] required to maintain the same value of P decreases from 8% (larger particle surface area) to 4% (smaller particle surface area) when t_s increases from 5 to 35 minutes. Thus, more particle nuclei will form during monomer addition if SDS is injected into the reaction medium earlier.

Three formulas (H, M, and L) were then selected to verify the predictive equation developed for P (Eq. 3). The recipes and experimental data are listed in

FIG. 1. Contour plot of P with $[\text{SDS}] = 1\%$.FIG. 2. Contour plot of P with $[\text{SDS}] = 2\%$.

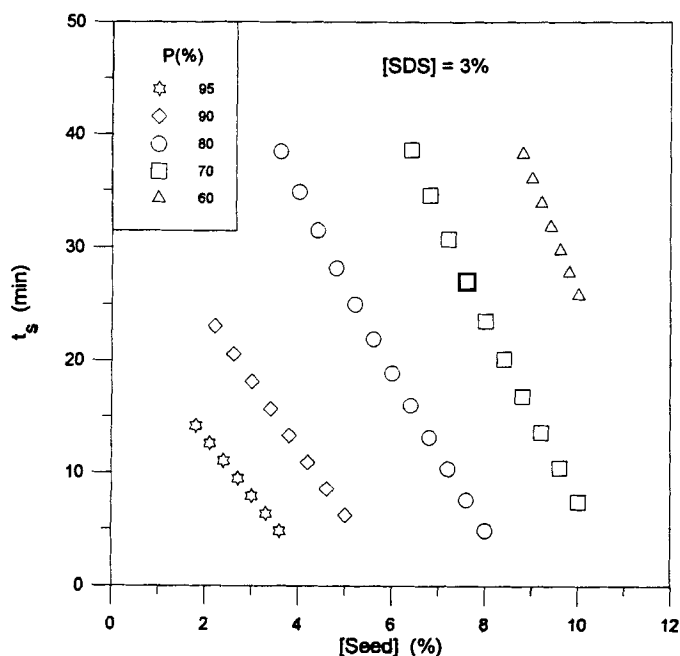


FIG. 3. Contour plot of P with $[\text{SDS}] = 3\%$.

Table 2. In this series of experiments, $[\text{SDS}]$ was kept constant at 3%. Experiments H and L were both carried out twice. Again, the reproducibility of these experiments is satisfactory. The total seed particle surface area (A_s) shown in Table 2 is calculated according to the following equation:

$$A_s = 6[\text{Seed}]W_m/(d_s\rho_s) \quad (4)$$

TABLE 2. Experiments to Verify the Predictive Equation of P

	H ^a	M	L ^a
Recipes:			
[Seed], %	2.50	5.35	7.45
t_s , min	10.52	22.61	31.23
[SDS], %	3	3	3
$A_s \times 10^{-6}$, cm ²	1.366	2.919	4.060
Results:			
d_f , nm	197 ± 12	318	349 ± 6
Predicted P , %	95.0	80.6	68.8
Experimental data	98.0 ± 0.4	82.1	67.1 ± 1.7
Error, %	3	2	3

^aData are the average of two identical experiments.

where ρ_s is the density of seed particles and has a value of approximately 1 g/cm^3 . The experimental data of P agree reasonably well with the predictions. These experiments support the above conclusion that the experiment with smaller values of $[\text{Seed}]$ (or A_s) and t_s favors formation of BPSD-Latices (see Table 2). Based on these experimental data, the validity of using Eq. (3) for predicting P was further confirmed.

Figures 4–6 show the d_p versus time (t) data for Experiments H, M, and L, respectively. The arrow indicated in the plot represents the time when an extra amount of SDS is injected into the reactor during monomer addition (t_s). The horizontal, dashed line in the plot indicates the seed particle size (d_s). Note that d_p represents an average particle size of the latex sample taken during monomer addition. Changes in d_p with t also reveal useful information on the particle size distribution. The d_p data shown in Fig. 4 are the average of two identical experiments for Formula H. Although the data are somewhat scattered, the trend that d_p increases to a maximum at $t \sim 120$ minutes (t_{max}) and then decreases rapidly as polymerization proceeds is definite. Immediately after injecting 3% SDS into the reactor ($t_s = 10.5$ minutes), the d_p data do not show any evidence of secondary nucleation. Figure 7(a) shows a typical latex particle size distribution at $t_{\text{max}} \sim 120$ minutes for Experiment H, in which a monodisperse distribution is observed. This does not rule out the existence of newly borne particle nuclei in the reaction system because these nuclei are extremely small ($< 30 \text{ nm}$) and their presence may not be detected by the dy-

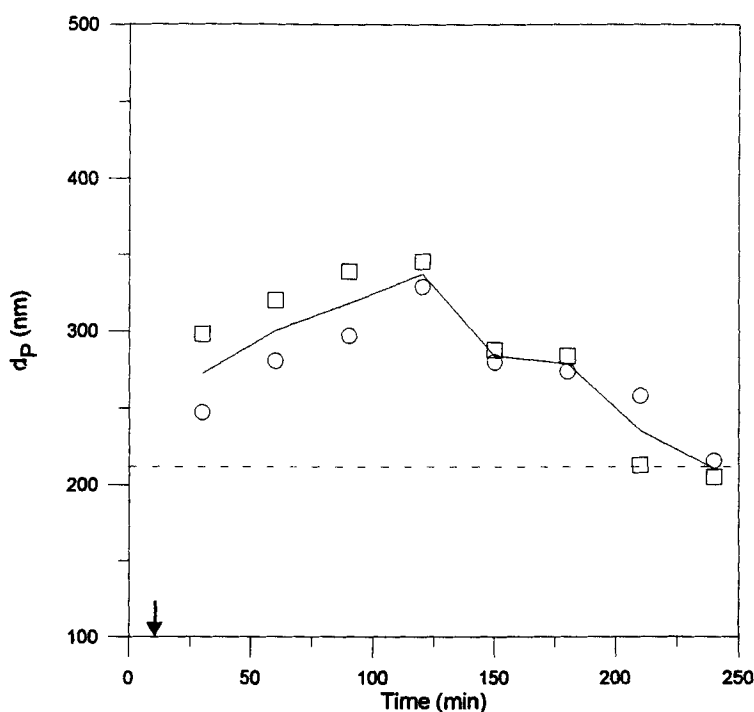


FIG. 4. Average latex particle size as a function of time for Experiment H.

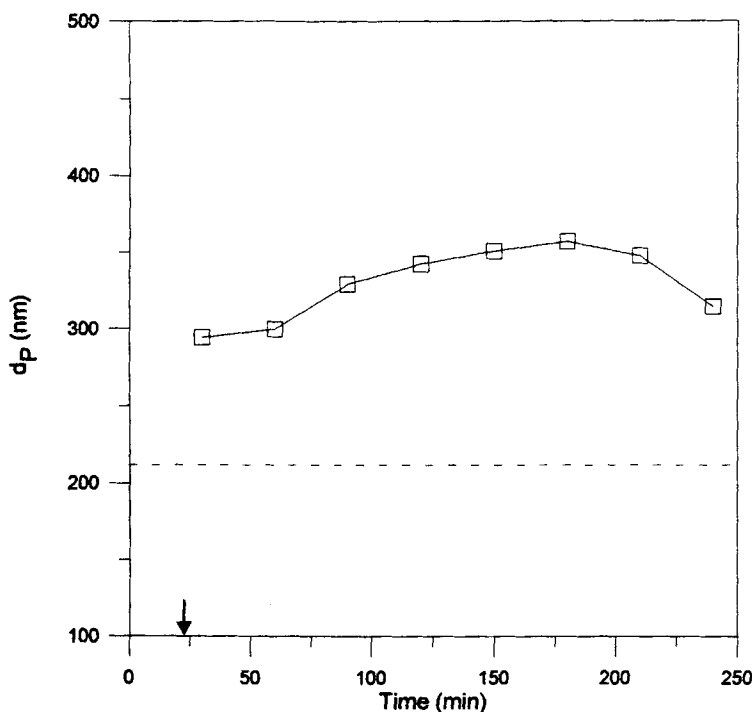


FIG. 5. Average latex particle size as a function of time for Experiment M.

namic light-scattering instrument. Furthermore, the equilibrium concentration of monomer in these particle nuclei is lower than that in seed particles ($d_s = 212$ nm) because of their very small radii of curvature. This may result in a slower polymerization rate (i.e., a slower particle growth rate) for these particle nuclei. This competitive growth mechanism further delays detection of primary particles originated from these particle nuclei. Thus, d_p increases monotonously up to 120 minutes. Subsequently, the population of tiny primary particles becomes significant and reflects in the decreased d_p data toward the end of polymerization (see Fig. 4). Figure 7(b) clearly shows a bimodal particle size distribution for the latex product H.

Figure 5 (Experiment M) shows that the maximal point occurs later in the reaction ($t_{\max} \approx 180$ minutes) when both [Seed] and t_s increase simultaneously (see Table 2). The maximum then becomes vague for Experiment L with the highest values of [Seed] and t_s (see Fig. 6). This trend implies the increased resistance to secondary nucleation with [Seed] and t_s . More particle nuclei produced by injecting SDS into the reaction medium are swept up by seed particles when [Seed] increases. In addition, not all the injected SDS molecules are available for stabilizing the generated particle nuclei. This is because a significant proportion of the injected SDS become adsorbed on the seed particle surface if the particle surface coverage is not saturated. Parameter t_s also has an influence on secondary nucleation. The larger the value of t_s , the greater is the seed particle-water interfacial area as more

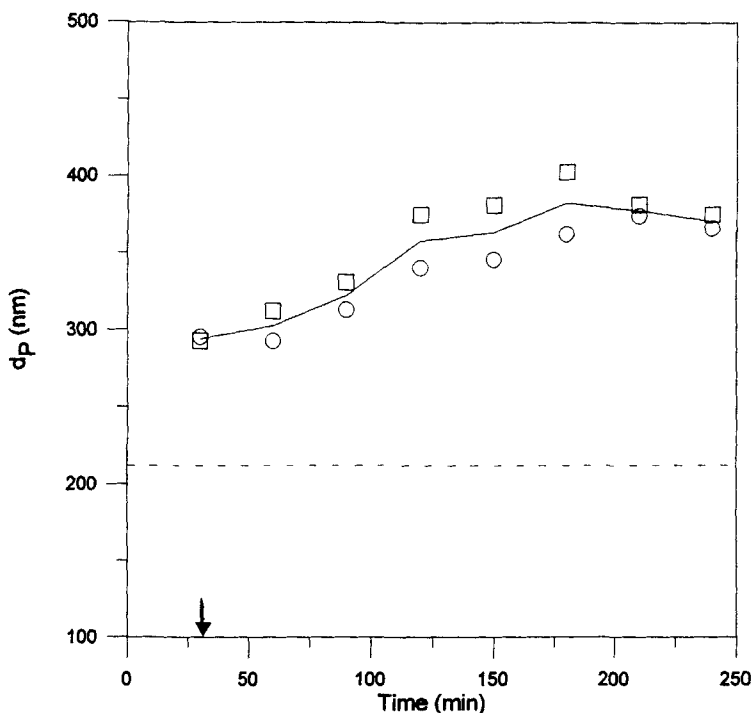


FIG. 6. Average latex particle size as a function of time for Experiment L.

monomer is polymerized inside the seed particles. This may thus cause a reduction in the number of particle nuclei generated later in the reaction. The corresponding particle size distribution data are shown in Figs. 8 (Experiment M) and 9 (Experiment L), respectively. The particle size distribution becomes narrower with increasing [Seed] or t_s (see Figs. 7–9). The particle size distribution data clearly show that Experiments H ($P = 98.0\%$) and M ($P = 82.1\%$) have a bimodal particle size distribution as shown in Figs. 7 and 8. However, the population of small particles, presumably caused by secondary nucleation, is not significant for Experiment L with $P = 67.1\%$ (see Fig. 9). BPSD-Latices may thus be produced if P is greater than approximate 70%. It can be concluded that the most efficient parameter in manipulating the latex particle size distribution is [Seed].

Based on Eq. (3), the calculated $\log P$ versus $\log[\text{Seed}]$ profiles at various values of t_s (5–35 minutes) are shown in Fig. 10. The value of [SDS] is set at 3% because t_s has the largest effect on P under this condition. Figure 10 shows that an empirical relationship such as $P \sim [\text{Seed}]^n$ is not applicable to the polymerization system. At constant t_s , the exponent n (i.e., rate of change in $\log P$ with $\log [\text{Seed}]$) decreases with increasing [Seed]. This implies the stronger resistance to formation of a second crop of tiny primary particles with increasing [Seed]. At constant [Seed], P decreases with increasing t_s , but the effect of t_s is less important in comparison with [Seed].

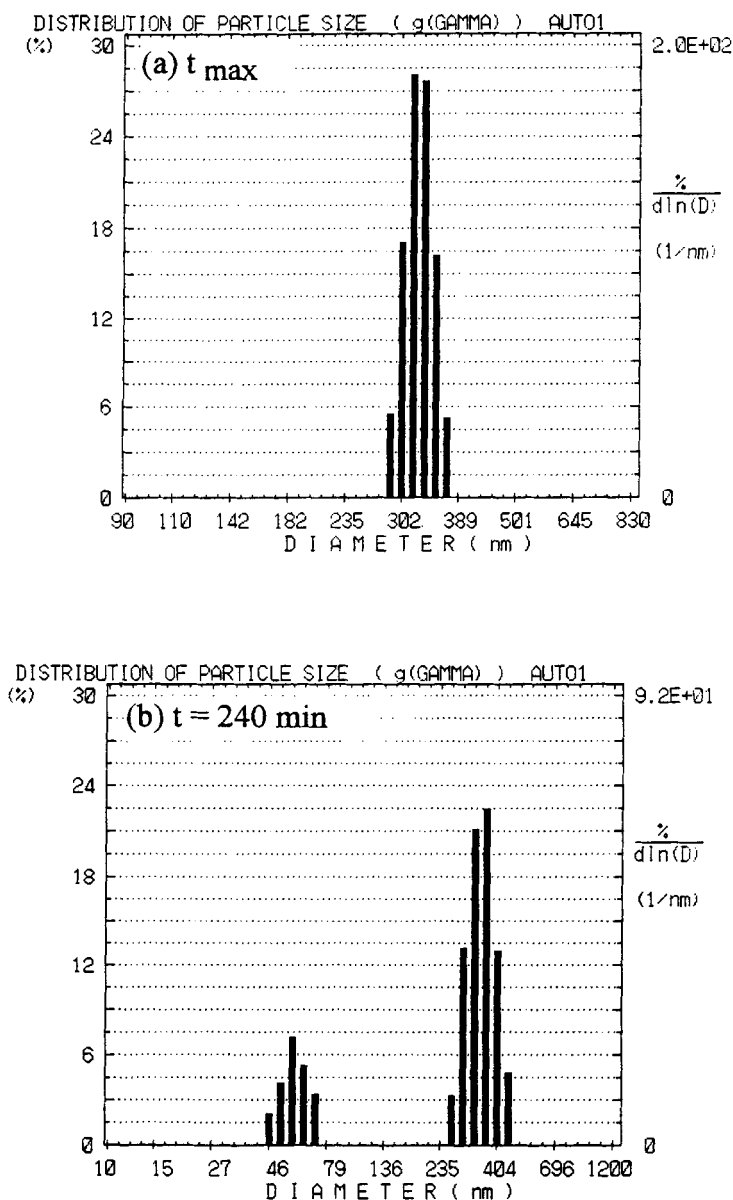


FIG. 7. Particle size distribution data for Experiment H.

Effect of Seed Particle Size

Another seed latex was prepared by a process similar to that used for the seed latex with $d_s = 212 \text{ nm}$. The only difference is that the mixture of 106.20 g H_2O , 1.06 g SDS, and 2.12 g NP-40 originally present in the monomer emulsion feed for preparing the seed latex with $d_s = 212 \text{ nm}$ was placed in the initial reactor charge to generate more particle nuclei (see the Experimental Section). The particle size, total

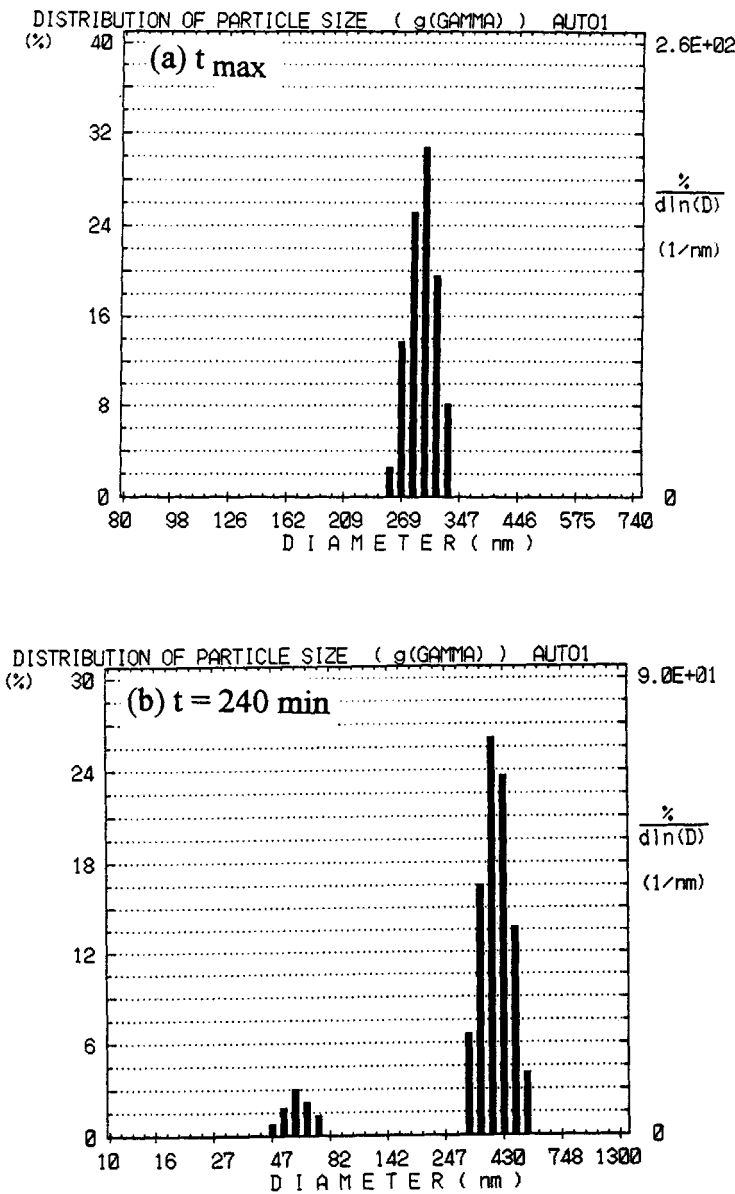


FIG. 8. Particle size distribution data for Experiment M.

solid content, and total scrap for the resultant seed latex are 88 nm, 30.6%, and 0.29%, respectively. This small seed latex was then used to replace the seed latex with $d_s = 212 \text{ nm}$ in Experiments H and L, respectively (designated as H' and L'). At constant weight of seed particles ($W_s = [\text{Seed}] W_m$), the total seed particle surface area (A_s) is inversely proportional to the seed particle size (d_s), as shown in Eq. (4).

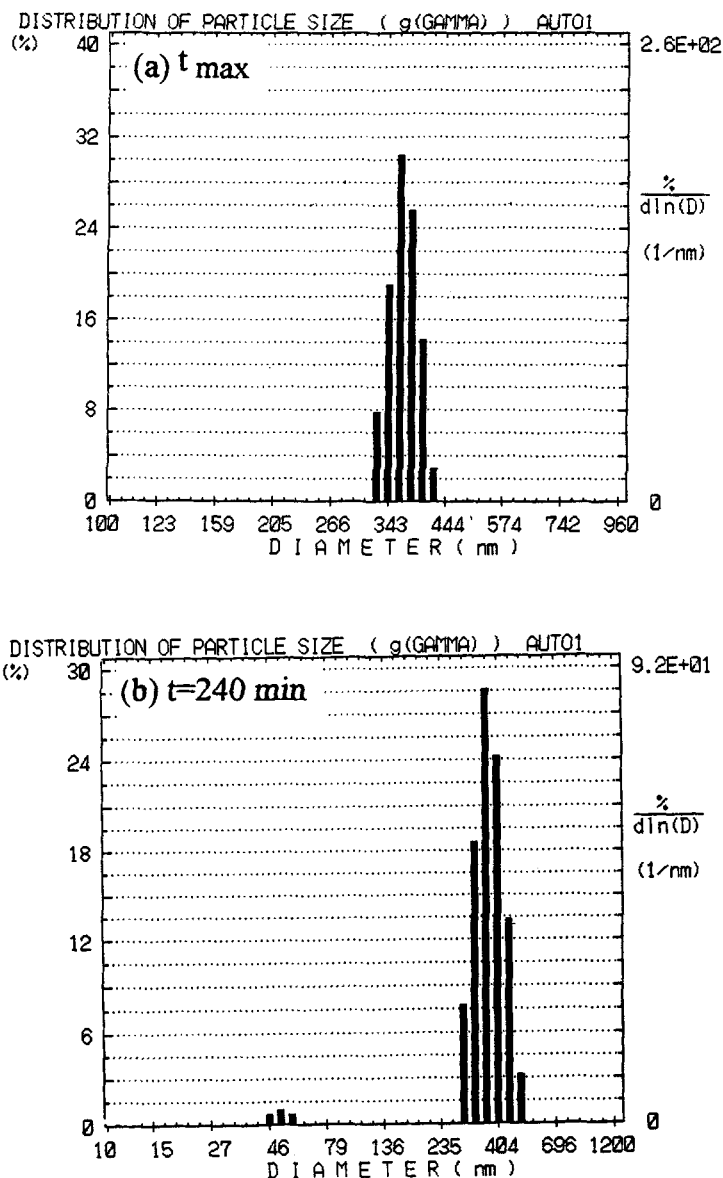


FIG. 9. Particle size distribution data for Experiment L.

Figure 11 shows the d_p versus t data for Experiments H' and L'. It is shown that d_p increases gradually with time, and no maximum is observed for either run. The values of A_s and P are $3.292 \times 10^6 \text{ cm}^2$ and 84.8% for Experiment H', and $9.781 \times 10^6 \text{ cm}^2$ and 53.5% for Experiment L', respectively. This result shows a similar trend that secondary nucleation is greatly retarded when [Seed] increases. Figure 11 shows that P (%) correlates well with A_s (cm^2) regardless of the seed particle size. Parameter P is proportional to A_s to the -0.319 power, which is

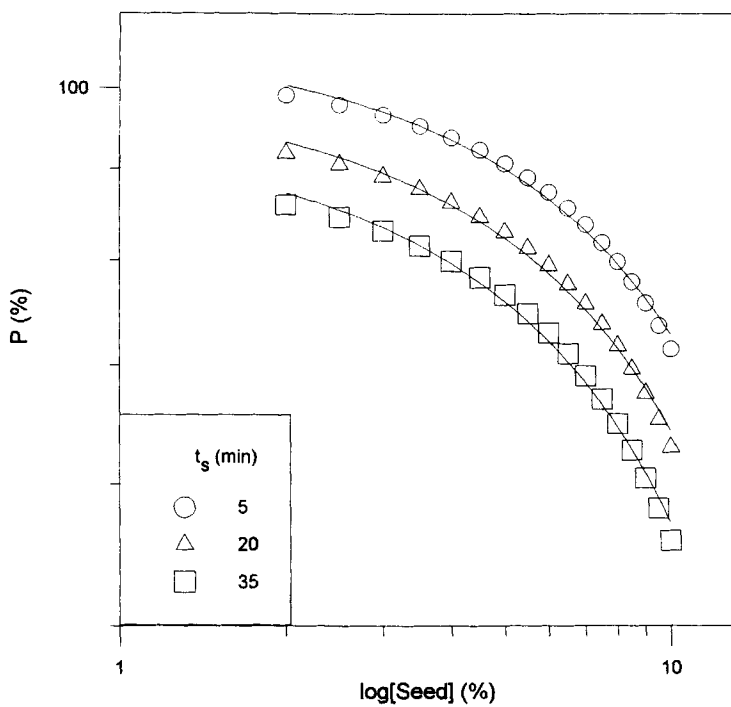


FIG. 10. Logarithmic plot of P as a function of weight percentage of seed particles.

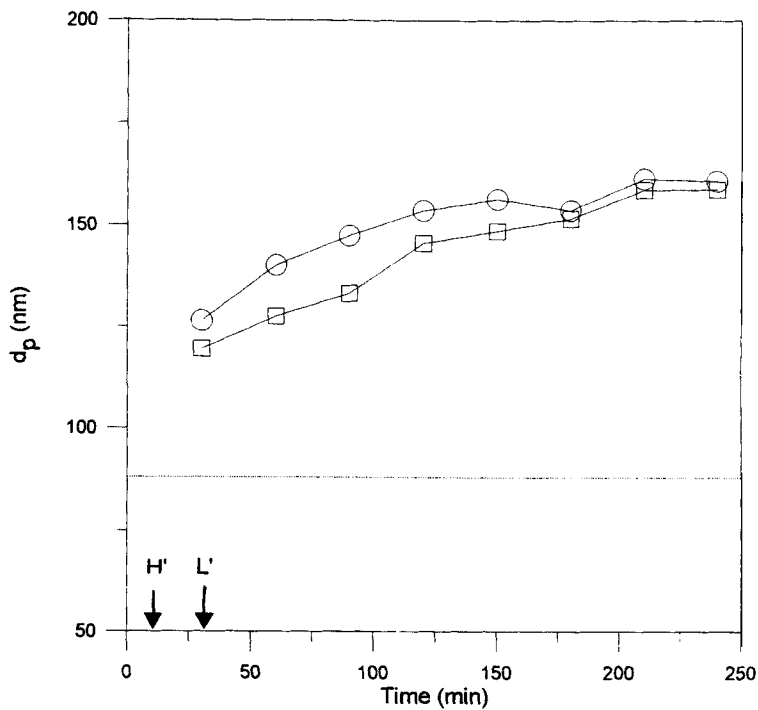


FIG. 11. Average latex particle size as a function of time for Experiments H' and L'.

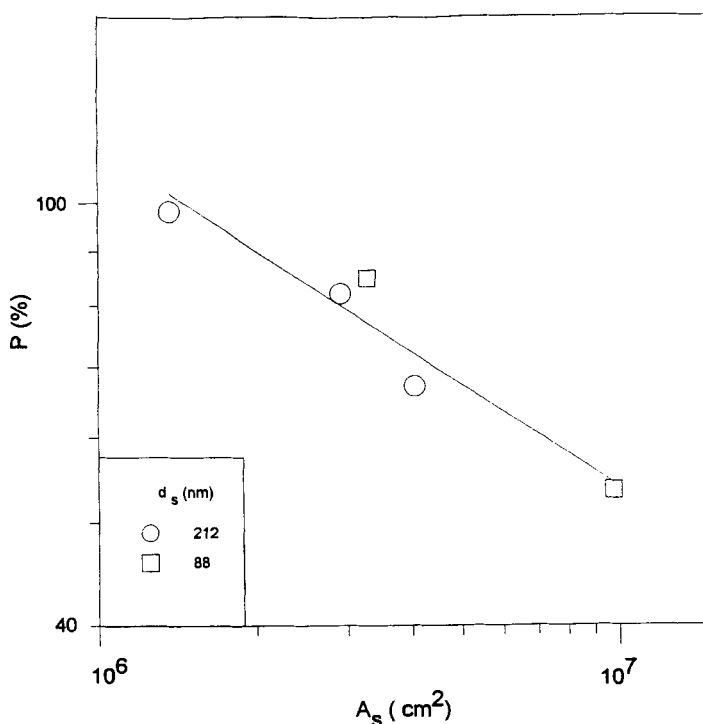


FIG. 12. Logarithmic plot of P as a function of total seed particle surface area.

obtained from the slope of the least-squares best fitted straight line in Fig. 12. Thus, the total seed particle surface area (A_s) is a universal variable for manipulation of the resultant latex particle size and particle size distribution.

CONCLUSIONS

Latex products with a bimodal particle size distribution (BPSD-Latices) can be prepared by injecting SDS into the reactor in the semibatch seeded emulsion polymerization of acrylic monomers. A two-level factorial design was used to study the effects of important variables on P , which is related to the final latex particle size and particle size distribution. The greater the value of P , the greater is the probability of nucleating a second crop of tiny primary particles (i.e., secondary nucleation) during monomer addition. The concentration of seed particles in the initial reactor charge ([Seed]) is the most important parameter for controlling P , followed by the time when SDS is injected into the reaction medium (t_s). The resultant latex particle size (d_p) is not sensitive to changes in the concentration of injected SDS ([SDS]). Parameter P decreases with increasing [Seed] or t_s . This implies retarded secondary nucleation during monomer addition when [Seed] or t_s increases. BPSD-Latices are best produced by the recipe with the lowest values of [Seed] and t_s .

Based on the factorial design, an empirical equation (Eq. 3) was developed to predict P . Three formulas (H, M, and L, shown in Table 2) were selected to verify the predictive equation. The experimental data agree reasonably well with the predictions. The data clearly show that Experiments H ($P = 98.0\%$) and M ($P = 82.1\%$) have a bimodal particle size distribution, as shown in Figs. 7 and 8. However, the population of small latex particles is not significant for Experiment L with $P = 67.1\%$ (see Fig. 9). BPSD-Latices may thus be produced if P is greater than approximately 70%. Furthermore, P correlates well with A_s , regardless of the seed particle size, and P (%) is proportional to A_s (cm^2) to the -0.319 power. Thus, A_s is a very useful variable for manipulation of the resultant latex particle size and particle size distribution.

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