

# **Influence of Monomer Preemulsification on Formation of Particles from Monomer Drops in Emulsion Polymerization**

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## **Synopsis**

Evidence was obtained supporting the theory that monomer droplets can become a locus of initiation and propagation in emulsion polymerization. This was done by reducing the size of the monomer droplets prior to initiation of polymerization using different preemulsification techniques for a typical latex recipe containing a common anionic surfactant. Monomer droplet size reduction caused an increase in the total surface area of the monomer droplets and thereby increased the competitiveness of these droplets for capturing active free radicals which are generated in the aqueous phase. As the total surface area of the monomer droplets was increased by preemulsification, a corresponding increase in the number of large particles formed by polymerization of these monomer droplets was experimentally measured. This work shows that monomer droplets are a locus of emulsion polymerization. However, the importance of monomer droplet polymerization is limited by their total surface area because of the competition for free radicals with other surfaces and/or particle nucleation processes. The results offer a basis for explaining why broad, and sometimes bimodal, particle size distributions are obtained in some commercial processes where the reactants are preemulsified prior to being charged into a reaction vessel.

## **INTRODUCTION**

The emulsification of a monomer (i.e., styrene) by simple mixing with an aqueous phase consisting of water and surfactant prior to initiation of emulsion polymerization produces an average monomer droplet diameter of about 30,000 nm. These droplets cannot effectively compete with monomer-swollen micelles (approximately 5 nm) for free radicals generated in the aqueous phase because of their significantly lower surface area.

This surface area ratio in a typical emulsion polymerization recipe will be approximately 1:100,000 (monomer droplet area:micelle area). As a consequence of this high ratio, monomer swollen micelles have long been accepted as the principal locus of initiation and propagation of emulsion polymerization, since the initial development of the Harkins theory.<sup>1</sup>

This theory is supported by the following phenomena: (1) The final concentration of latex particles is greater than the initial concentration of emulsion droplets. (2) The size of the final particles is much smaller (by an order of magnitude) than the emulsion droplets.

It has been shown in recent papers by Ugelstad et al.<sup>2-5</sup> that monomer droplets may become the main locus for initiation of polymerization if the droplet size is reduced far enough using mixed emulsifier systems of anionic or cationic surfactants and long-chain fatty alcohols. It has not been reported in the liter-

ature whether monomer droplets may serve as a locus of polymerization in a typical latex recipe using a simple anionic surfactant. That was the objective of this study.

At the onset of this experiment, it was hypothesized that if the surface area of the monomer droplets could be increased by preemulsifying the aqueous and monomer phases—prior to initiation—these droplets might become a more significant locus of polymerization and result in a bimodal particle size distribution. The effect of droplet size on the surface area of 1 g monomer is shown in Table I. As the size of the monomer droplets are reduced from 30,000 nm, which is typical of gently charged emulsion polymerization samples, to the range of 1500 nm to 1000 nm, which is near the minimum size attainable with surfactants such as Aerosol MA, the surface area per particle will decrease, but the total surface area per unit volume will increase by a factor of 20 to 30.

## EXPERIMENTAL

### Materials

Commercial-grade styrene monomer (Dow Chemical Company) was used after distillation under reduced pressure. Commercial grades Aerosol MA-80% (American Cyanamid Company), reagent-grade sodium bicarbonate (Lehigh Valley Chemical Company), certified-grade potassium persulfate (Fisher Scientific Company), and grade-5 nitrogen gas (Air Reduction Company) were all used without further purification.

### Preparation of Latexes

The polymerization recipe used in this study is identified in Table II. Four degrees of preemulsification were utilized in the polymerization recipe. To ensure uniformity of the solutions for each of the preemulsified samples, stock

TABLE I  
Monomer Droplet Surface Area

Droplet diameter, nm	Total surface area nm <sup>2</sup> /g	Emulsification technique
30,000	$2.20 \times 10^{17}$	gently charged
15,000	$4.40 \times 10^{17}$	hand shaking <sup>6</sup>
7,000	$9.45 \times 10^{17}$	homogenization <sup>7</sup>
3,000	$2.20 \times 10^{18}$	homogenization <sup>7</sup>
1,500	$4.40 \times 10^{18}$	ultrasonification <sup>8</sup>
1,000	$6.61 \times 10^{18}$	ultrasonification <sup>8</sup>

TABLE II  
Polymerization Recipe

	Parts
Styrene	20
Water	65
Persulfate initiator	0.10
Bicarbonate buffer	0.10
Aerosol MA surfactant	0.65

solutions of the aqueous phase (water, surfactant, buffer) and the initiator solution (water, potassium persulfate) were prepared. The aqueous phase for each of the four samples was weighed from these stock solutions. The monomer was weighed and added to the aqueous phase to complete the emulsion recipe for each sample. The samples were then preemulsified as follows. Method 1, no preemulsification (control); Method 2, hand shaking the bottle 100 times vigorously; Method 3, homogenized two times, using a Fisher Scientific brand hand homogenizer; Method 4, Ultrasonified, using a Sonifier brand ultrasonifier Model "Cell Disrupter" for 30 sec at setting No. 5 and 10% duty cycle.

Following preemulsification, the emulsions were transferred to 4-oz glass bottles fitted with screw caps containing self-sealing gaskets ("sandwich" of B. F. Goodrich W-7 butyl rubber, and W-9/50:50 PVC-SBR mixture). The atmosphere of each bottle was purged with Airco ultrapure grade nitrogen for 5 min by inserting two hypodermic syringes through the gasket material. The potassium persulfate solution (from common stock solution) was then injected through the gasket material to initiate polymerization. The polymerization was carried out to high conversion (95-98%) at 70°C for 24 hr, tumbling end-over-end in a safety basket at 30 rpm.

### Characterization of Latexes

Following polymerization, it was desirable to isolate the large particles and determine their relative number. Concentration of the large particles was accomplished by a series of centrifugation steps using a Sorval Superspeed Centrifuge. Particle diameter measurements were made using electron microscopy.

Nine ml of each sample was placed in a centrifuge tube and spun for 15 min. The top 7 ml of the samples was then pipetted out and replaced with distilled water and the latex was redispersed by shaking and spun for another 15 min. The bottom 1 ml was then removed, diluted to a known concentration, and an electron microscope grid prepared with a known volume of liquid on the grid. By assuming all large particles in the original 9-ml sample were spun down into the final 1 ml, it was possible to obtain a "semiquantitative" number of large particles in the sample. This was accomplished by back calculating, through all of the dilution steps, from the number of large particles counted on the electron microscope grid.

The total mass of large particles in the sample was calculated from the "semiquantitative" number of large particles, the size distribution of the large particles, and the density of the polymer. By assuming that all of the particles in the sample belonged to either the large or small particle fractions, it was possible to calculate the number of small particles, using a mass balance around each sample and the size distribution of small particles.

## RESULTS AND DISCUSSION

Table III shows the total number of large particles determined in each sample for the recipe using Aerosol MA as the emulsifier. It is evident from these data that, as the surface area per unit volume of the monomer droplets is increased 20 to 30-fold by variation of the preemulsification method (Table I), the number

TABLE III  
 Frequency of Large Particles

Sample	Number of particles/cm <sup>3</sup>		Weight ratio large particle/ small particle
	Large	Small	
No preemulsifier	$7.84 \times 10^5$	$2.15 \times 10^{13}$	$0.33 \times 10^{-6}$
Hand shaking	$1.68 \times 10^6$	$2.25 \times 10^{13}$	$1.01 \times 10^{-6}$
Ultrasonification	$2.24 \times 10^7$	$1.38 \times 10^{13}$	$17.3 \times 10^{-6}$
Homogenization	$1.98 \times 10^7$	$7.35 \times 10^{13}$	$63.90 \times 10^{-6}$

of large particles measured experimentally is increased 28.6-fold. The weight ratio of small/large particles per unit volume is insignificant in these polymerizations, even when the monomer droplet size is reduced to the 1- $\mu$ m range. This suggests that, if preemulsification of the monomer and aqueous phases is not needed to eliminate the formation of coagulum or to increase the mass transfer rates, this step could be eliminated from the process.

Table IV gives some additional data on these four samples. One point to note from these data is the difference in the dispersity between the small and large particle distributions. A much larger dispersity is expected and observed in the particles formed by initiation in monomer droplets because of the nonuniformity of the site, as opposed to the particles initiated by the conventional mechanisms. No experiments were performed to determine the effect of preemulsification on the rate of polymerization, but this work could be of interest.

## SUMMARY

This work shows that initiation and propagation of emulsion polymerization can occur in monomer droplets when a simple anionic emulsifier system is used; however, the number of large particles formed is limited by the relatively small surface area of the monomer droplets and therefore is very small.

These results also offer an explanation for the broad, and sometimes bimodal, particle size distributions obtained in some commercial processes where the reactants are preemulsified before being charged into a reaction vessel.

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TABLE IV

	No preemulsification	Hand shaking	Homogenization	Ultrasonification
Conversion, %	97.9	97.9	93.7	98.9
Final pH	6.7	6.7	6.7	6.7
Small particles				
No. avg. diameter, nm	269	265	176	313
Dispersity rate	1.007	1.004	1.017	1.016
Large particles				
No. avg. diameter, nm	563	630	1,190	726
Dispersity rate	1.245	1.037	1.193	1.313

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