

In Situ Surfactant Generation as a Means of Miniemulsification?

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ABSTRACT: *In situ* emulsification, where the surfactant is synthesized spontaneously at the oil/water interface, has been put forth as a simpler method for the preparation of miniemulsions-like systems. Miniemulsions are relatively stable oil-(e.g., monomer)-in-water emulsions having droplet sizes anywhere in the range of 50–500 nm, and are typically created with high shear and stabilized by the combination a surfactant and a costabilizer. Using the *in situ* method of preparation, emulsion stability and droplet and particle sizes were monitored and compared with conventional emulsions and miniemulsions. Styrene emulsions prepared by the *in situ* method do not demonstrate the stability of a comparable miniemulsion. Upon polymerization, the final particle size generated from the *in situ* emulsion did not differ significantly from the com-

parable conventional emulsion polymerization; the reaction mechanism for *in situ* emulsions is more like conventional emulsion polymerization rather than miniemulsion polymerization. Similar results were found when the *in situ* method was applied to controlled free radical polymerizations (CFRP), which have been advanced as a potential application of the method. Molecular weight control was found to be achieved via diffusion of the CFRP agents through the aqueous phase owing to limited water solubilities. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 735–745, 2009

Key words: miniemulsions; *in situ* emulsification; particle size distribution; kinetics (polym.); emulsion polymerization

INTRODUCTION

One of the major differences between miniemulsion and conventional emulsion polymerization systems is the locus of particle nucleation. Soap micelles are the typical locus in conventional emulsion systems; on the other hand, it is monomer droplets in miniemulsions owing to their small size resulting from the method of preparation of miniemulsions and the use of a costabilizer. Since the application of high shear typically causes an increase in the total surface area of the monomer droplets in miniemulsions, they can compete effectively for free radicals during polymerization. The large surface area of the monomer droplets is a consequence of their small size and stability against coalescence and diffusional degradation (Ostwald ripening). Surfactant is used to prevent the former, whereas a low-molecular weight, low-water solubility costabilizer is used to retard the latter.^{1,2}

In miniemulsion systems, the final particle size can be controlled by the initial droplet size since particle

formation takes place in the monomer droplets. Some authors have claimed that droplets in miniemulsion polymerization have the same size and distribution as the final particles, which supports the concept of a one-to-one copy from monomer droplets to polymer particles.³ Although this one-to-one mechanism is not usually operative, more direct control of particle size and size distributions is possible with miniemulsion polymerization compared with conventional emulsion polymerization.^{2,4,5}

Emulsification includes two main steps: first, increasing the surface area by deformation and breakage of the monomer phase creating droplets, and second, the stabilization of these droplets by using surfactants (and costabilizer in the case of miniemulsions). Cetyl alcohol was used as costabilizer in early miniemulsion studies and simple mixing using a magnetic stir bar was sufficient to form stable miniemulsion droplets.^{6–8} However, the energy obtained from simple mixing was not sufficient to produce small and homogeneously dispersed monomer droplets, when hexadecane was applied as costabilizer. Higher energy, at least higher than the difference in surface energy between the interfacial tension and the newly formed interface, was required to obtain droplets with large surface area.⁹ Homogenization devices are most often used for miniemulsion preparation to produce this

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required high energy. Sonifiers, high pressure homogenizers, and rotor-stator systems are the most common homogenization devices. The high pressure homogenizers are the most efficient devices to create small droplets.^{10–12}

An *in situ* emulsification process has been described as a simplifying alternative method to generate miniemulsion-like systems in terms of droplet size without the need of high shear mixing and a costabilizer.^{13,14} In this method, the driving force to form droplets is said to be chemical instead of mechanical.¹⁵ When a monomer emulsion is obtained spontaneously with the synthesis of an emulsifier at the monomer-water interface, the emulsification method is termed "*in situ*." In this process, latent surfactant such as oleic acid is first dissolved in the monomer and an aqueous solution containing a base, such as potassium hydroxide, is added and the surfactant (potassium oleate) is spontaneously formed at the interface and an emulsion forms.

Many experimental and theoretical studies have been carried out investigating the interfacial tension in acidic oil/alkaline solution systems. The interest in this process was due to its applications in enhanced oil recovery where an alkaline aqueous solution is used to flood a crude oil reservoir to emulsify and extract the oil.^{16–21} These studies showed that the acids present in the oil phase react with the alkaline solution to produce *in situ* surfactants that lower the interfacial tension between oil and water. At the minimum interfacial tension, slight agitation can result in immediate emulsification.

Propokov and Gritskova^{15,22} also proposed that this *in situ* procedure results in the formation of an emulsion that has a much lower interfacial tension than an emulsion prepared by a conventional method, since the emulsifier formed in the neutralization reaction is accumulated in the interfacial layer. The emulsions prepared by this method are reportedly 5–10 times more stable than those obtained from preformed surfactant/monomer mixtures, and the average diameter of the monomer droplets is about two times smaller because the monomer droplet size and stability depends on interfacial tension. The difference in interfacial tensions is illustrated by data from the literature, reproduced in Figure 1, where the *in situ* method produces significantly lower styrene/aqueous phase values.¹⁵

During the preparation of the surfactant at the interface, acid first diffuses from the oil phase to the interface and is adsorbed; the neutralization reaction then occurs at the interface followed by the desorption of the surfactant from the interface into the aqueous phase.^{21–23}

This work critically evaluates the *in situ* emulsification method as a possible alternative to miniemul-

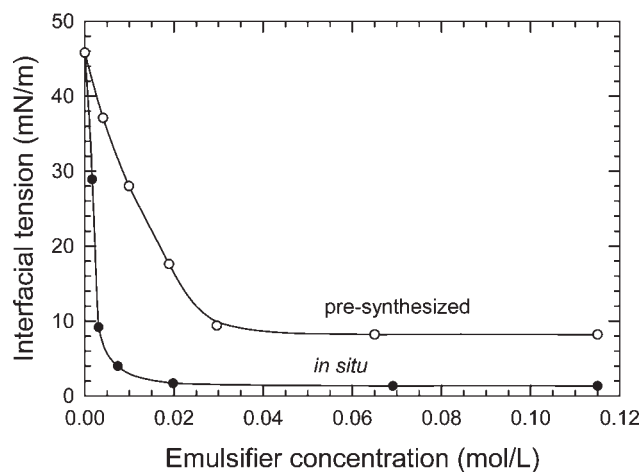


Figure 1 Interfacial tension at the interfaces between: (1) aqueous solution of potassium laurate and styrene, and (2) aqueous solution of potassium hydroxide and styrene solution of lauric acid as a function of emulsifier concentration.¹⁵

sion technology in terms of emulsion stability and droplet size, as well as the resulting particle size upon polymerization. It is compared with both conventional emulsification and miniemulsion methods. The mechanism of polymerization is examined in both free radical and controlled free radical polymerizations.

EXPERIMENTAL

Materials

Styrene (Sigma-Aldrich) monomer was purified via vacuum distillation in the presence of cuprous chloride at a pressure of 35 mmHg at 55°C to remove inhibitor and any oligomers. The monomers were refrigerated before use. Lauric acid (Acros) or oleic acid (Sigma-Aldrich) and potassium hydroxide (KOH; Fisher Scientific) were used to synthesize the surfactant (i.e., potassium laurate or potassium oleate). Potassium persulfate (KPS; Sigma-Aldrich) was used as initiator in the polymerization reactions. Hexadecane (HD; Sigma-Aldrich) or cetyl alcohol (CA; Aldrich) was used as costabilizer. *N-tert-butyl- α -phenylnitron* (PBN; Sigma-Aldrich) and dibenzyltrithiocarbonate (DBTTC; Arkema) were used as control agents in controlled radical polymerization experiments. Deionized (DI) water was used for all emulsions.

Emulsion preparation

Emulsions were prepared to observe their stability and to measure the droplet size. The basic recipe used is given in Table I. The emulsions for stationary tests were prepared by the *in situ* emulsification method where the surfactant was spontaneously

TABLE I
Recipe Used for *In Situ* Emulsion Stability Studies

Ingredient	Weight (g)
Styrene	20.00
DI water	37.14
Lauric acid (114 mM) ^a	0.85
KOH (129.56 mM) ^a	0.27
NaHCO ₃ (91.66 mM) ^a	0.29
HD or CA ^b	0.72

^a Based on aqueous phase.

^b Only used for experiments with costabilizer.

synthesized at the interface. The oil phase was prepared by dissolving lauric acid in monomer (styrene) and the aqueous phase, including KOH, sodium bicarbonate, and DI water, was added to the oil phase at 65°C. Miniemulsions are formed by mixing the aqueous solution of potassium laurate with the styrene/HD oil phase at room temperature and sonifying (Branson sonifier, Model 450, at a power level of 7 and 60% duty cycle) for 10 min.

Two *in situ* emulsions were prepared under different conditions. The first emulsion was prepared by simple mixing with a magnetic stir bar at 65°C and the other one was sonified for 10 min using the sonifier at a power level of 7 and 60% duty cycle. Differences in the appearance of the emulsions were usually noted to judge the emulsion stability.

For droplet size measurements, three different methods were used to prepare the emulsions. First, the emulsions were prepared with the formation of surfactant at the interface (*in situ*). Second, emulsions were formed upon emulsification of the monomer in an aqueous solution of the surfactant (presynthesized surfactant). Third, monomer with costabilizer (hexadecane) present was mixed with an aqueous solution of the surfactant and sonified (miniemulsion). Droplet sizes were measured with the acoustic particle sizer (APS; Model 100, Matec Applied Sciences). The recipe given in Table I is scaled up by a factor of 2.5 for these experiments since a relatively large amount of emulsion is required (~140 mL) for the APS measurement. Droplet sizes are reported as number-average droplet size (D_n), area-average droplet size (D_a), and polydispersity index (PDI).

To investigate the effect of costabilizer on the stability and droplet size, emulsions utilizing hexadecane and cetyl alcohol were prepared, where the costabilizer was added to the oil phase before emulsification. The amount of the costabilizer used is also given in Table I.

Polymerization reactions

Polymerizations were run both in a bottle polymerizer unit and in a stirred reactor. The procedure was

TABLE II
Recipe Used For Styrene Bottle Polymerizations

Ingredient	Weight (g)
<i>In situ</i>	
Oil phase	
Styrene	15.000
Lauric acid (114 mM) ^a	0.6375
HD or CA ^b	0.5400
Aqueous phase	
DI water	27.855
KOH (129.56 mM) ^a	0.2025
NaHCO ₃ (91.66 mM) ^a	0.2145
KPS	0.0900
Pre-synthesized surfactant	
Oil phase	
Styrene	15.000
HD or CA ^b	0.5400
Aqueous phase	
Lauric acid (114 mM) ^a	0.6375
DI water	26.145
KOH (129.56 mM) ^a	0.2025
NaHCO ₃ (91.66 mM) ^a	0.2145
KPS Solution	
KPS	0.5000
DI water	9.5000

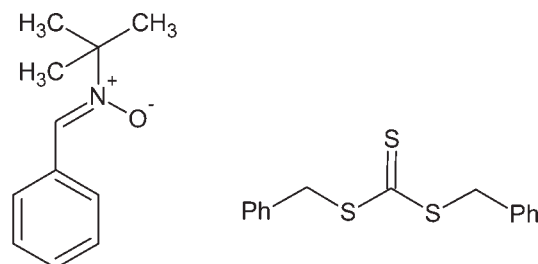
^a Based on aqueous phase.

^b Only used for experiments with costabilizer.

basically the same for both of the methods. The details of these experiments are given in the following subsections.

Bottle polymerization

The recipe used in the bottle polymerization experiments is given in Table II. For the *in situ* method, first, the aqueous phase and oil phase were prepared separately and placed in 60-mL glass bottles with septum stopper and then the bottles were purged with nitrogen. The aqueous phase was loaded into a syringe and added to the oil phase bottle (~1 mL/s), while the bottle was purged with nitrogen and stirred with a magnetic stirrer. After replacing the septum stopper with a Teflon-lined cap, this mixture was placed in the bottle polymerizer with end-over-end rotation (32 rpm) at 65°C.



N-*tert*-Butyl- α -phenylnitron

Dibenzyltrithiocarbonate

Figure 2 Structures of the two free radical control agents.

TABLE III
In Situ Recipe Used for Controlled Radical Polymerizations with *N*-*tert*-Butyl- α -Phenylnitron (PBN)

Ingredient	Weight (g)
Oil phase	
Styrene	7.50
Oleic acid	0.450
PBN	0.075
Aqueous phase	
DI water	30.00
KOH	0.123
K ₃ PO ₄	0.300
KPS	0.300

For the presynthesized surfactant method, first, the aqueous and oil phases and initiator (KPS) solution were prepared in separate 60-mL glass bottles. In preparing the aqueous phase, lauric acid and potassium hydroxide (KOH) were dissolved in DI water by mixing for at least 30 min. Second, the aqueous phase was added via syringe to the oil phase bottle, while purging with nitrogen and stirring with a magnetic stirrer. Then 1.8 g of KPS solution was added to the emulsion. After purging the final mixture with nitrogen for 30 s, it was placed in the bottle polymerizer at 65°C.

Stirred reactor polymerization

A 250-mL four-neck round-bottom flask equipped with a mechanical paddle stirrer, nitrogen inlet, condenser, thermometer, and injection (sampling) port was used for the stirred reactor polymerizations. The reactor was placed in a thermostated water bath set at 65°C. For *in situ* reactions, the oil phase was charged into the reactor and allowed to reach the set point temperature. The aqueous phase was then injected as a thin stream (~ 1 mL/s) into the organic solution using a syringe and needle. For the presynthesized surfactant method, the oil and aqueous phases were both charged into the reactor and after reaching the set point temperature, 5.4 g initiator (KPS) solution was added to the reactor. The recipe given in Table II was scaled up by a factor of 3 for the stirred reactor polymerizations. The impeller

TABLE IV
In Situ Recipe Used for Controlled Radical Polymerization Reactions with Dibenzyltrithiocarbonate (DBTTC)

Ingredient	Weight (g)
Oil phase	
Styrene	30.0
Oleic acid	1.80
DBTTC	0.45
Aqueous phase	
DI water	55.7
KOH	0.40
NaHCO ₃	0.43
KPS	0.18

speed was around 100 rpm for all of these experiments.

Particle size analysis

Capillary hydrodynamic fractionation (CHDF; Model 2000, Matec Applied Sciences) was used to determine the particle size. The samples were diluted to ~ 0.5 wt % with eluent and filtered through nylon filters (5 μ m) prior to injection into the CHDF. Particle sizes are reported as number-average particle diameter (D_n), volume-average particle diameter (D_v), and polydispersity index (PDI).

Controlled free radical polymerizations

Two different controlled free radical polymerization reactions (CFRP) were performed to examine the mechanism of the polymerization using the *in situ* emulsification method.^{13,14} The first, employed *N*-*tert*-butyl- α -phenylnitron (PBN) as the radical control agent in bottle polymerizations,²⁴ whereas the second used dibenzyltrithiocarbonate (DBTTC) as control agent in a stirred reactor.¹³ The structures of these two free radical control agents are shown in Figure 2, while the recipes for these experiments are given in Tables III and IV, respectively.

For polymerizations with PBN, first styrene, oleic acid, and PBN were added to a 60-mL bottle. After flushing with nitrogen, a solution of K₃PO₄, KOH,

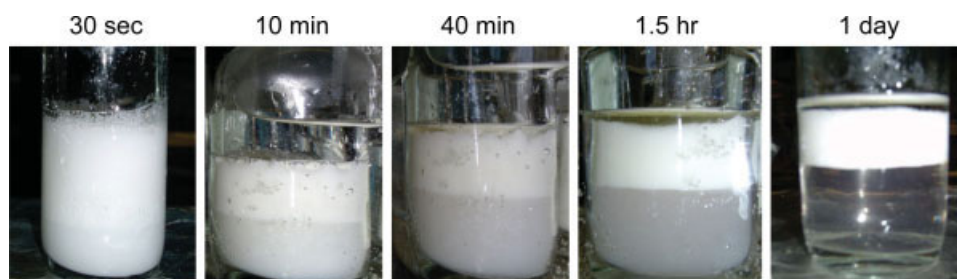


Figure 3 Appearance as a function of time of an emulsion formed by mixing an aqueous solution of potassium hydroxide with a styrene/lauric acid oil phase (65°C).

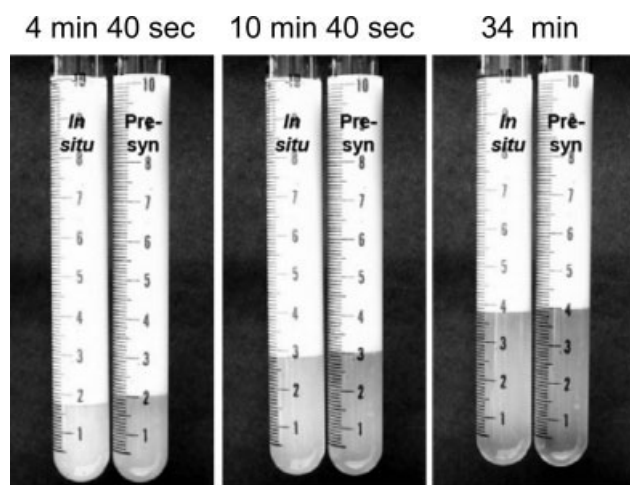


Figure 4 Creaming as a function of time for emulsions formed by *in situ* and presynthesized surfactant methods at room temperature.

and KPS was added with stirring. Bottles were flushed with nitrogen and placed into the bottle polymerizer set at 75°C. For polymerization reactions with DBTTC, a 250-mL four-necked round-bottom flask equipped with a mechanical paddle stirrer, nitrogen inlet, condenser, thermometer, and injection (sampling) port was used. Styrene, oleic acid, and DBTTC were charged into the reactor and flushed with nitrogen. Aqueous phase was prepared by dissolving KPS, NaHCO₃, and KOH in DI water and added to the stirred oil phase as a thin stream. The reaction was run at 65°C for 5 h. The final latexes were analyzed using CHDF for particle size and gel permeation chromatography (GPC) for molecular weight. For GPC analysis, samples were dried at room temperature and then dissolved in THF (0.5 wt %). The solutions were then filtered through a 0.45- μ m filter before injecting into the GPC.

RESULTS AND DISCUSSION

Stability measurements

The emulsions formed by mixing the aqueous solution of potassium hydroxide with the styrene/lauric acid oil phase were observed at 65°C over time, as shown in Figure 3. Here it is seen that the emulsion is not very stable, contrary to what was reported in the literature. Phase separation (creaming) was observed almost immediately and after 40 min, a separate oil layer formed on top of the creamed white emulsion layer. After 1 day, the bottom layer was transparent indicating that no Brownian droplets were present.

Emulsions were prepared by both *in situ* and presynthesized surfactant methods and placed in graduated test tubes to observe their stability and to compare their separation rates. Figure 4 shows these

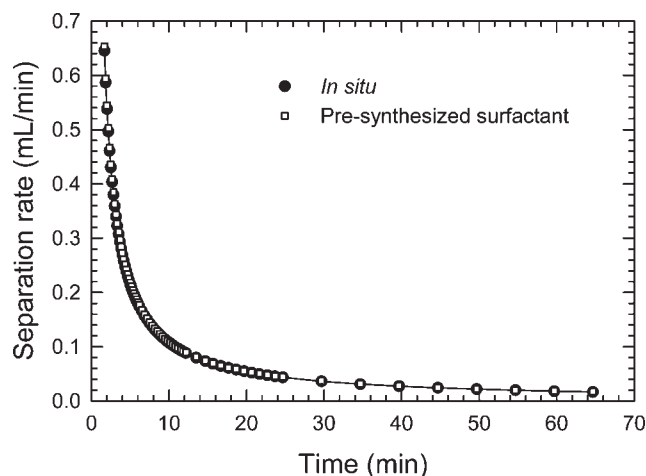


Figure 5 Separation rate versus time of emulsions formed by *in situ* and presynthesized surfactant methods at room temperature.

emulsions at different times. The emulsion in the left tube of each photograph was prepared by the *in situ* method, mixing the aqueous potassium hydroxide solution with the styrene/lauric acid oil phase. In contrast, the emulsion in the right tube was prepared by mixing the presynthesized aqueous potassium laurate solution with styrene. These emulsions were prepared at room temperature by stirring for 10 min. As can be seen, separation (creaming) of both emulsions is almost the same, indicating that the partitioning of the surfactant is similar for the two systems. To calculate separation rates, the volume of the creamed phase was measured as a function of time for both emulsions. The separation rates are plotted versus time in Figure 5. The same separation rate profile was obtained for both emulsions,

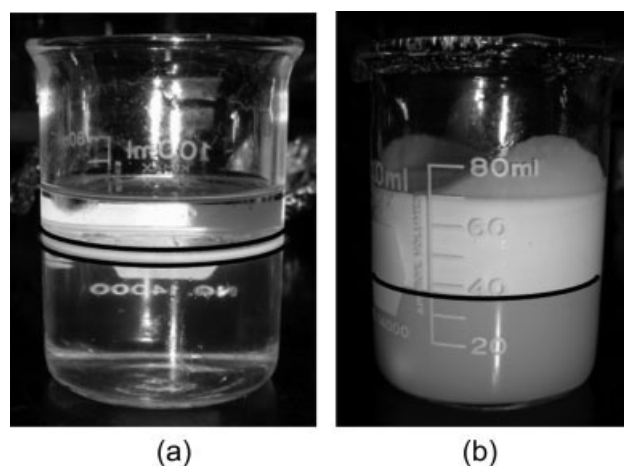


Figure 6 Emulsions formed from an aqueous solution of potassium hydroxide and a styrene/lauric acid oil phase after 4 days: (a) formed by simple stirring with a magnetic stir bar at 65°C, and (b) formed via sonification.

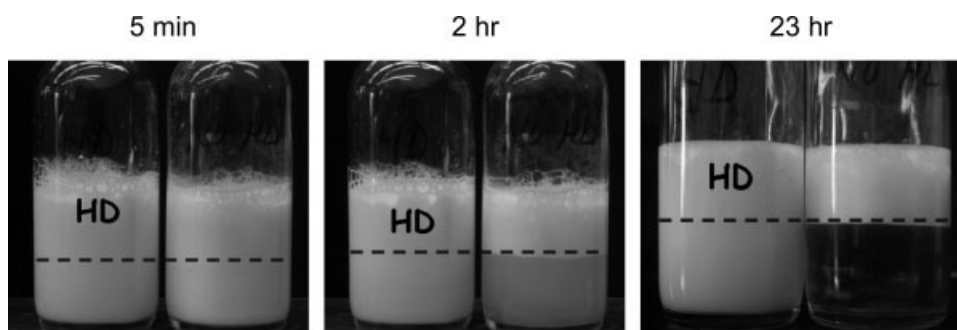


Figure 7 Change in the appearance of emulsions prepared with and without hexadecane as a function of time at room temperature.

which means that the *in situ* preparation method did not improve the stability of these emulsions.

Figure 6 shows two emulsions formed from an aqueous solution of potassium hydroxide and a styrene/lauric acid oil phase. On the left, the emulsion was formed by simple stirring and on the right, it was formed by sonification (Branson sonifier, Model 450, at a power level of 7 and 60% duty cycle) for 10 min. As can be seen by the thin white band (lines drawn on images to highlight phase divisions), after 4 days only a very small portion of sample (a) remained as an emulsion, while the sonified sample (b) had a relatively large fraction of emulsion.

A low-molecular weight, low-water solubility costabilizer is used in miniemulsions, along with a surfactant, to stabilize the droplets by reducing the extent of droplet degradation by Ostwald ripening. To investigate the effect of the presence of costabilizer on the same system, emulsions were prepared by mixing an aqueous solution of potassium hydroxide with a styrene/lauric acid/HD oil phase at room temperature using a magnetic stirrer. Phase separation of the emulsions was observed over time, as shown in Figure 7. The left sample in each photograph contains hexadecane (HD), whereas the right one has none. Although both emulsions exhibited phase separation, the bottom layer was clearer when hexadecane was not used. Apparently, the presence of hexadecane slows phase separation and makes the emulsions more stable. This observation may also imply that some small droplets were formed during the emulsification, which was stabilized by the presence of hexadecane.

Since the *in situ* preparation method has been proposed as an alternative for miniemulsion systems, the stability of these systems were compared by observing the separation of emulsions prepared by *in situ* and miniemulsion methods. Figure 8 shows the creaming of these emulsions over time. The miniemulsion in the left tube of each photograph was formed by mixing the aqueous solution of potassium laurate with the styrene/HD oil phase at room temperature and sonifying (Branson sonifier, Model 450,

power level of 7 and 60% duty cycle) for 10 min. The *in situ* emulsion in the right tube was prepared by mixing an aqueous solution of potassium hydroxide and a styrene/lauric acid oil phase where the surfactant was synthesized at the interface. Although creaming was observed within minutes for the emulsion prepared by the *in situ* method, the miniemulsion showed no sign of creaming for weeks. If the *in situ* emulsion containing HD (Fig. 7) and miniemulsion (Fig. 8) are compared, it can be seen that even when HD is included, the *in situ* method does not provide the same stability as a miniemulsion.

Droplet size of emulsions prepared by different methods

If the emulsion is prepared under conditions where emulsifier is synthesized at the interface, Prokopov and Gritskova¹⁵ proposed that the average size of the droplets will be two times smaller than the comparable conventional emulsion. To observe the effect

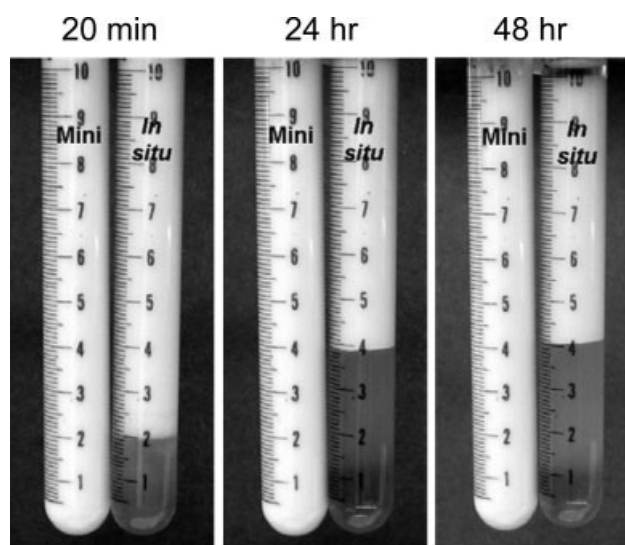


Figure 8 Creaming as a function of time for emulsions formed by *in situ* and miniemulsion methods at room temperature.

TABLE V
Average Droplet Size Values (from APS analysis) for Emulsions Prepared by Various Methods

Method	D_n (μm)	D_a (μm)	PDI
<i>In situ</i>	10.6	11.1	1.12
Presynthesized surfactant	13.5	15.4	1.28
<i>In situ</i> with HD	3.7	14.4	4.54
Miniemulsion	0.06	0.10	4.33

of the emulsion preparation method on droplet size, the emulsions were analyzed by APS on the same day as the preparation. The first emulsion was prepared by the *in situ* method, while the other was prepared by the presynthesized surfactant method. The droplet size averages are given in Table V. An optical micrograph of the emulsion prepared by the *in situ* method can be seen in Figure 9. Although the droplet size is smaller when the surfactant is synthesized at the interface, still the difference is not double. In addition, the micron-size droplets confirm that the system is not "miniemulsion-like." The droplet size of emulsions prepared by the *in situ* method is also compared with the droplet size of miniemulsions prepared using the same surfactant to further confirm that the two systems are not comparable. As can be seen from Table V, miniemulsion droplets are much smaller than the *in situ* droplets.

The effect of HD on the droplet size was also studied by adding HD into the oil phase before the emulsification. The smaller value for the number-average diameter indicates that some smaller droplets were produced in the emulsion system when prepared by the *in situ* method. However, they are still micron-size and well outside the range of a classical miniemulsion system.

Polymerization reactions

Polymerizations were first performed in a bottle polymerizer unit and then in a stirred reactor. For the bottle polymerization, the reaction temperature and the reaction time were 65°C and 5 h, respectively. To compare the particle sizes of the latexes prepared by

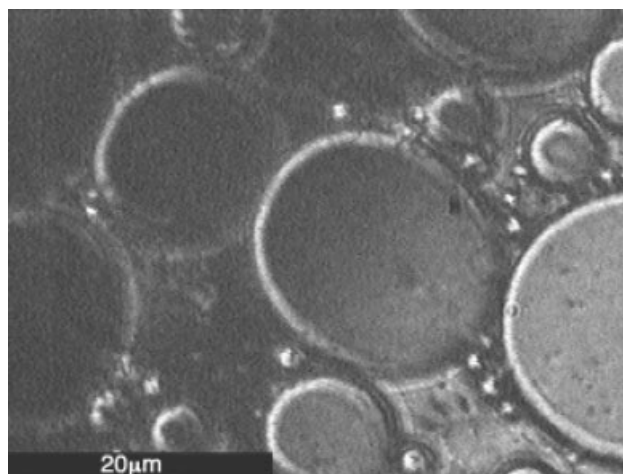


Figure 9 Optical micrograph of styrene emulsion droplets prepared by the *in situ* method.

the *in situ* and the presynthesized surfactant methods, styrene was polymerized using potassium laurate or potassium oleate as surfactant. In the first method, surfactant was synthesized at the interface from the reaction of lauric acid or oleic acid in the oil phase and KOH in the aqueous phase. In the second method, the preformed surfactant was added to the aqueous phase before the emulsification. The pH of the final latexes for all cases was between 8 and 9. The particle size, conversion, and solids content of the final latexes were measured and are given in Table VI. No significant differences are observed between the particle sizes of the polystyrene latexes prepared by the *in situ* and the presynthesized surfactant methods. The particles are all ~ 70 nm in size regardless of the method used to prepare the initial emulsions. This small particle size combined with the large droplet sizes reported earlier clearly implies that nucleation does not take place in droplets but rather in the aqueous phase; in this case, this is considered to be primarily in micelles.

The costabilizers, hexadecane and cetyl alcohol, were added in separate experiments to the oil phase prior to emulsification (as in miniemulsion polymerization) to see if there was any effect on the particle size of the final latex. As can be seen from Table VI,

TABLE VI
Comparison of Final Polystyrene Latexes Prepared by Bottle Polymerization Using Different Methods and Surfactants

Method	Surfactant	Particle size			Solids %	Conv %
		D_n (nm)	D_v (nm)	PDI		
<i>In situ</i>	Potassium laurate	70 \pm 3	72 \pm 5	1.06	35.5 \pm 1.0	97.2 \pm 2.0
Pre-synthesized surf		70 \pm 1	71 \pm 1	1.05	36.2 \pm 0.4	97.4 \pm 0.5
<i>In situ</i>	Potassium oleate	75 \pm 2	77 \pm 1	1.08	36.9 \pm 0.1	99.0 \pm 0.5
Pre-synthesized surf		71 \pm 3	72 \pm 4	1.07	36.1 \pm 0.1	97.3 \pm 1.0
<i>In situ</i> with HD	Potassium laurate	70 \pm 2	72 \pm 2	1.25	36.2 \pm 0.2	97.5 \pm 0.4
<i>In situ</i> with CA		71 \pm 1	73 \pm 1	1.08	38.3 \pm 0.2	98.2 \pm 1.0

TABLE VII
Comparison of Final Polystyrene Latexes Prepared in Stirred Reactor Using Different Methods and Surfactants

Method	Surfactant	Particle size			Solids %	Conv %
		D_n (nm)	D_v (nm)	PDI		
<i>In situ</i>	Potassium laurate	68 ± 2	68 ± 2	1.04	35.6 ± 0.2	97.5 ± 0.9
Pre-synthesized surf		61 ± 1	62 ± 1	1.03	30.1 ± 0.2	81.6 ± 0.5
<i>In situ</i>	Potassium oleate	74 ± 1	75 ± 1	1.06	36.4 ± 0.1	98.2 ± 1.0

the addition of either costabilizer did not change the particle size significantly.

After obtaining the same particle size by both methods, the polymerization procedure was taken into consideration. In bottle polymerization, the emulsions were prepared at room temperature and then the reaction temperature (65°C) was reached in the bottle polymerizer unit. Since the *in situ* method involves synthesis of surfactant spontaneously at the time the emulsion is prepared, the time difference between preparing the emulsions and starting the polymerization reaction may lead to differing results. This situation is thought to be one possible reason for obtaining the same mean particle size for both cases. For that reason, further polymerization reactions were run in a stirred reactor.

The results for the styrene polymerizations in a stirred reactor are given in Table VII. The reaction temperature was 65°C and the reaction time was 5 h. As can be seen from this table, the method of adding the surfactant into the system did not change the particle size. The presurfactant method required more time to reach the same conversion as the *in situ* method, which explains the smaller particles (lower conversion).

Kinetics of the styrene polymerization when the surfactant is synthesized at the interface

The kinetics of styrene emulsion polymerization when the surfactant (potassium laurate) was synthe-

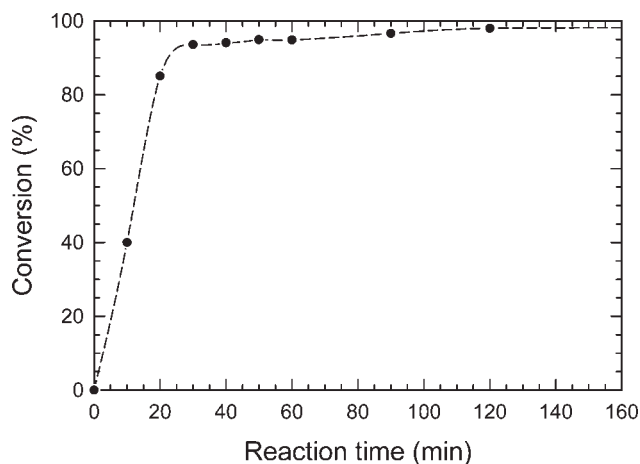


Figure 10 Conversion as a function of reaction time for styrene emulsion polymerization where the surfactant (potassium laurate) was synthesized at the interface.

sized at the interface was studied using a 250-mL four-neck round-bottom flask reactor at 65°C. The results are shown in Figure 10. Within 20 min, 85% of the styrene was converted to polymer and after 30 min the conversion was about 94%. The particle size of the latex was also measured as a function of time using CHDF. The results in Table VIII show that the size of the polystyrene particles did not change significantly with time, particularly after 10 min reaction as would be expected from the kinetics.

Styrene emulsion polymerization with an alternative recipe

Propokov and Gritskova²⁵ used a different recipe in styrene polymerizations where the *in situ* method was applied. For this reason, the recipe used in the previous experiments (Recipe 1), which was taken from the study of Parker,¹³ was modified as reported in Table IX. Recipe 2 is lower in monomer, initiator, and emulsifier. Polymerizations were performed in a 250-mL stirred reactor at 65°C where the surfactant (potassium laurate) was synthesized both at the interface and before emulsification. Conversion and particle size were determined as a function of time as shown in Figure 11 and Table X. Results show that for this recipe, the particle size is larger and the reaction rate slower compared to the previous styrene emulsion polymerization. The decrease in

TABLE VIII
Conversion and Particle Size as a Function of Reaction Time for Styrene Emulsion Polymerization where the Surfactant (Potassium Laurate) was Synthesized at the Interface

Time (min)	Particle size			Conv %
	D_n (nm)	D_v (nm)	PDI	
10	61.1	61.7	1.03	40.00
20	64.6	73.0	1.10	85.06
30	66.0	67.1	1.05	94.08
40	65.5	66.9	1.11	93.59
50	64.6	65.6	1.05	94.91
60	65.3	66.3	1.05	94.85
90	65.3	66.4	1.05	96.59
120	65.7	66.9	1.06	97.98
180	65.6	66.7	1.05	98.17
240	66.5	67.8	1.06	98.86
300	64.8	66.0	1.06	99.57

TABLE IX
Comparison of Different Recipes Used for Styrene Emulsion Polymerizations

	Recipe 1	Recipe 2
Volume ratio of monomer water phases	0.60	0.10
Initiator concentration (wt % based on aq phase)	0.32	0.10
Emulsifier concentration wrt aqueous phase (wt %)	2.72	0.25
Reaction time (h)	5	5

emulsifier concentration, which is close to the cmc (0.22 wt %),²⁵ explains the larger particle size and slower rate (fewer particles). The reference study gives the particle size as 182 nm,²⁵ which is the size we obtained after 3 h reaction; however, at that time the conversion had only reached 40%.

The results are also compared with those obtained by the presynthesized surfactant method where the surfactant (potassium laurate) was synthesized before the emulsification process. These results are also given in Figure 11 and Table X. Again, larger (fewer) particles resulted in a slower rate of polymerization. The evolution of the number of particles (N_p) was calculated from particle size data, for these systems and is given in Figure 12. A similar decrease in N_p is observed for both *in situ* and presynthesized surfactant systems. Since the surfactant level is relatively low in this recipe, the particles may not be well-stabilized, which causes some limited aggregation leading to the decreasing of number of particles.

Controlled free radical polymerization

CFRP is used to control polymer structure by means of control over molecular weight, polydispersity, and monomer sequences. The transport of the control agent within the reaction system is an important issue for heterogeneous CFRP reactions. Poor transport (very low water solubility) of the control agent can limit the control over the reaction depending on

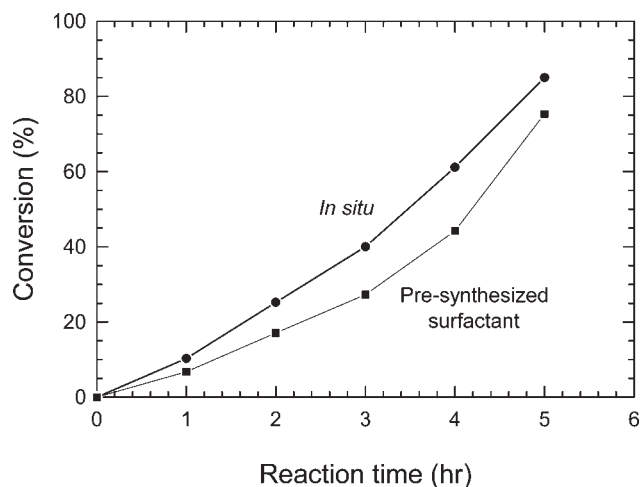


Figure 11 Conversion as a function of reaction time for the styrene emulsion polymerizations carried out with Recipe 2 (Table IX) where the *in situ* and presynthesized surfactant (potassium laurate) were employed.

its location (i.e., monomer droplets versus polymer particles). To overcome this problem several techniques have been developed. Miniemulsions have been used prominently in CFRP and have met with considerable success.^{26,27} As a simple alternative, *in situ* emulsification has been proposed for use in CFRP reactions instead of miniemulsions.²⁴ A few controlled radical polymerization experiments were performed in this study to see how effective the *in situ* emulsification method is in carrying out CFRP. Up to this point, it has been seen that *in situ* emulsification method is not a good alternative to miniemulsions in polymerization reactions. Its performance with free radical control agents will be evaluated next.

The first reaction was performed via using *N*-tert-butyl- α -phenylnitron (PBN) as radical control agent. Polymerization was run via bottle polymerization at 75°C for 6 h. The final particles were analyzed in terms of diameter and molecular weight, and the results are given in Table XI. As can be seen, the molecular weight of the polystyrene obtained from

TABLE X
Conversion and Particle Size as a Function of Reaction Time for Styrene Emulsion Polymerizations using Recipe 2 (Table IX) Where the *In situ* and Presynthesized Surfactant (Potassium Laurate) were Employed

Time (h)	<i>In situ</i>				Presynthesized surfactant			
	Particle size			Conv %	Particle size			Conv %
	D_n (nm)	D_v (nm)	PDI		D_n (nm)	D_v (nm)	PDI	
1	109.2	110.4	1.03	10.28	102.45	103.9	1.04	6.75
2	158.1	150.2	1.02	25.19	144.45	145.8	1.03	17.07
3	180.8	182.4	1.02	40.02	166.45	168.7	1.04	27.28
4	221.9	222.7	1.01	61.13	205.2	206.4	1.02	44.21
5	260.4	261.4	1.01	85.00	286.1	286.75	1.01	75.34

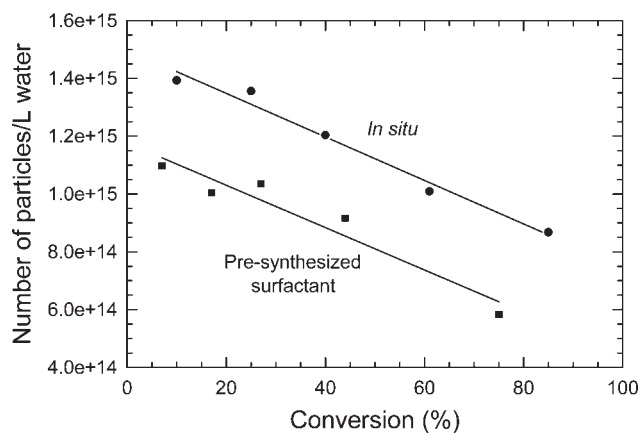


Figure 12 Number of particles as a function of conversion for the styrene emulsion polymerizations carried out with Recipe 2 (Table IX) where the *in situ* and presynthesized surfactants (potassium laurate) were employed.

the reaction with PBN is much lower than the molecular weight of polystyrene prepared without PBN indicating that the control agent does regulate the molecular weight in this system.

Since the transport of control agent can be important for its effectiveness, an experiment was designed to test the diffusivity of PBN in the system. For this experiment two emulsions were prepared, one with and one without PBN. These two emulsions were mixed together just before placing them in the bottle polymerizer. The molecular weight of the final latex was measured to determine whether it had a bimodal distribution or not. If it gave a bimodal distribution where one population has a high molecular weight as would be produced without the radical control agent, then that would indicate that the control agent has a poor diffusivity in the system. If the molecular weight distribution is not bimodal, then PBN can diffuse readily and the reaction is not limited by poor diffusion. The molecular weight distribution for this reaction is given in Figure 13 along with both previous polymerizations with and without PBN. Since the distribution is not bimodal and is similar to the previous reaction with

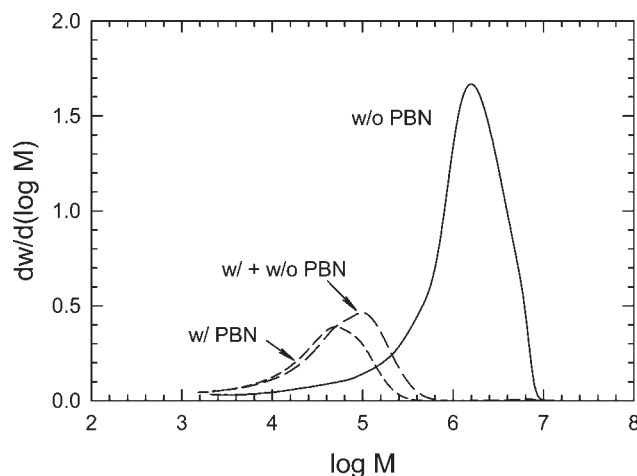


Figure 13 Molecular weight distributions of polystyrene produced in reactions with PBN, without PBN, and by mixing two emulsions that were prepared with and without PBN.

PBN, the controlled radical polymerization is clearly not diffusion limited. These obviously represent lower molecular weights than produced without PBN and show that molecular weight control is achieved when the *in situ* emulsification method is used.

A second free radical control agent, dibenzyltrithiocarbonate (DBTTC), was used in polymerizations carried out in a stirred reactor at 65°C for 5 h.¹³ The molecular weight and particle diameter results can be seen in Table XII. The results are consistent with the literature values. DBTTC is also a good control agent for these systems and like PBN does not suffer from any diffusion limitations as well.

CONCLUSIONS

Emulsions prepared by the *in situ* method do not demonstrate the stability of a comparable miniemulsion; phase separation can be observed within minutes. Adding a costabilizer such as hexadecane slows down the phase separation, implying an increased stability. When the droplet size of emulsions prepared by both the *in situ* method and pre-surfactant method are measured, it is observed that

TABLE XI
Conversion, Particle Size (CHDF), and Molecular Weight Data (GPC) for Emulsion Polymerizations of Styrene with and without PBN as a Radical Control Agent

	With PBN	Without PBN
Particle diameter		
D_n (nm)	60.6 ± 1	74.0 ± 1
PDI	1.02	1.06
Molecular weight		
M_n (g/mol)	Parker ¹³ = 33,060 32,600 ± 1000	517,600 ± 1000
PDI	1.87	3.70
solids %	22.4 ± 0.1	36.1 ± 0.1
Conversion %	98.0 ± 0.1	99.0 ± 0.2

TABLE XII
Conversion, Particle Size (CHDF) and Molecular Weight Data (GPC) for Controlled Radical Polymerization of Styrene where DBTTC was used as a Radical Control Agent

Particle diameter		Molecular weight		Solids	Conv
D_n (nm)	PDI	M_n (g/mol)	PDI	%	%
75.5 ± 1	1.25	16,318	1.53	35.9 ± 0.1	96 ± 0.5
		26,000 ¹³	1.13 ¹³		

the droplet size is large (in the micron range) in both cases. The *in situ* method gives smaller droplets, although the difference is not double as reported in the literature. The particle size of the final polystyrene latexes is small (~ 70 nm) and is not affected by the emulsion preparation method, either *in situ* or presurfactant. The combination of large droplet size with small particle size indicates that the reaction mechanism for *in situ* emulsions is more like conventional emulsion polymerization instead of miniemulsion polymerization where the droplets are the loci for particle nucleation. *In situ* emulsification without high shear and a costabilizer is not an alternative for miniemulsions. On the other hand, the molecular weights of the polystyrene obtained from the CFRP reactions with both PBN and DBTTC are much lower and narrower than the molecular weight of polystyrene prepared without radical control agent indicating that the control agents do act to control the molecular weight when the *in situ* emulsification method is used. This occurs because of sufficient water solubility of these control agents allowing them to diffuse to the loci of polymerization.

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