

# Particle Nucleation Mechanism for the Emulsion Polymerization of Styrene with a Novel Polyester Emulsifier

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**ABSTRACT:** The particle nucleation mechanism in emulsion polymerization of styrene with a novel polyester emulsifier, 5-sulfoisophthalic acid dimethyl ester sodium salt-modified tetracarboxylic acid-terminated polyester (SMTAPE), was investigated. The consumption of SMTAPE micelles was monitored by the measurement of surface tension during the emulsion polymerization. Kinetic studies and emulsifier consumption clearly showed that a continuous nucleation mechanism without Smith–Ewart interval II was characteristic of this system. It was attributed to the high concentration of SMTAPE emulsifier in the polymerization, which led to a large surface area and a vast number of micelles around 10 nm in size that served as the major locus of particle nucleation. A broad particle size distribution was observed throughout the reaction, and the nucleation period lasted well into the reaction until the disappearance of the micelles or the disappearance of monomer droplets. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1061–1070, 2001

**Key words:** polyester; emulsifier; emulsion polymerization; nucleation; latex

## INTRODUCTION

Polymeric emulsifiers provide many significant benefits to the latex industry, including low foaming, good chemical and mechanical stability, rheology modification, and improved coating quality.<sup>1–4</sup> Previous investigations have developed block or graft amphiphatic polymeric emulsifiers, polyelectrolytes, and polysoap emulsifiers.<sup>5–10</sup> Among the various polymeric emulsifiers, polyester-based emulsifiers are of paramount concern.<sup>3,4,11–13</sup>

Almost all previous studies of polymeric emulsifiers have focused on the structural design of the molecules. Furthermore, several characteristics of using polymeric emulsifiers in emulsion polymerization have been demonstrated. The first is that the diffusion rate of a polymeric emulsifier molecule in an aqueous solution is fairly low compared with the rates of traditional low molecular weight emulsifiers,<sup>4,8</sup> and several micelles lead to a final latex particle.<sup>7,8</sup> In addition, micellar nucleation is involved in polymerizations with polymeric emulsifiers.<sup>6,9</sup>

In conventional emulsion polymerization for a low-water-soluble monomer, the monomer is emulsified into the continuous aqueous phase, monomer droplets 1–10  $\mu\text{m}$  in size are formed,

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and most of the emulsifiers are either dissolved in the continuous phase or are in the form of micelles. The large total surface area of the micelles compared with the area of the monomer droplets greatly favors the micelles in the initial absorption of aqueous-phase-formed free radicals. In such systems, the three intervals of Smith–Ewart kinetics are clearly indentifiable.<sup>14,15</sup> For the micellar entry mechanism, the rate of polymerization ( $R_p$ ) in interval II can be expressed as follows:

$$R_p = K_p \bar{n} N_p [M]_p / N_a$$

where  $K_p$  is the propagation rate coefficient,  $N_p$  is the number of polymer particles,  $[M]_p$  is the concentration of monomer in the polymer particles,  $\bar{n}$  is the average number of radicals per particle, and  $N_a$  is Avogadro's number.  $N_p$  is determined by the concentrations of the initiator and emulsifier ( $[S]$ ) and the reaction temperature.

There are two systems that can create small monomer droplets to provide a large surface area. The first one is miniemulsion polymerization, in which an effective emulsifier–coemulsifier system is used and very small (10–500 nm) monomer droplets are stabilized.<sup>15–18</sup> Another one is microemulsion polymerization, in which thermodynamically stable monomer droplets and monomer-swollen micelles about 10 nm in size are formed.<sup>18–23</sup> In those systems, nucleation is primarily via radical entry into the monomer droplets. The reaction then proceeds by the polymerization of monomer in the monomer droplets, new particles are formed continuously during the reaction, and no true Smith–Ewart interval II is observed.

The 5-sulfoisophthalic acid dimethyl ester sodium salt (SSIPM)-modified tetracarboxylic acid-terminated polyester (SMTAPE) emulsifier has been used to produce acrylic latices.<sup>24–27</sup> Such latices have high reaction rates and high polymer molecular weights and possess low coagulum and good mechanical stability. The SMTAPE emulsifier can be dispersed in small micelles (8–20 nm) in an aqueous solution with good stability.<sup>26</sup> The goals of this study were to determine the particle nucleation mechanism when SMTAPE was used in the emulsion polymerization of styrene and to investigate the related reaction kinetics.

## EXPERIMENTAL

### Materials

Materials used in this study included styrene monomer (Acros), potassium persulfate (Jans-

sen), potassium hydroxide (Tedia), diethylene glycol (Tedia), isophthalic acid (Lancaster), and SSIPM (TIC). All the chemicals were reagent-grade and were used as received, except for the styrene monomer. The inhibitor was removed from the styrene by its passage through an aluminum oxide packed column. The water was deionized.

### Synthesis of the SMTAPE Emulsifier

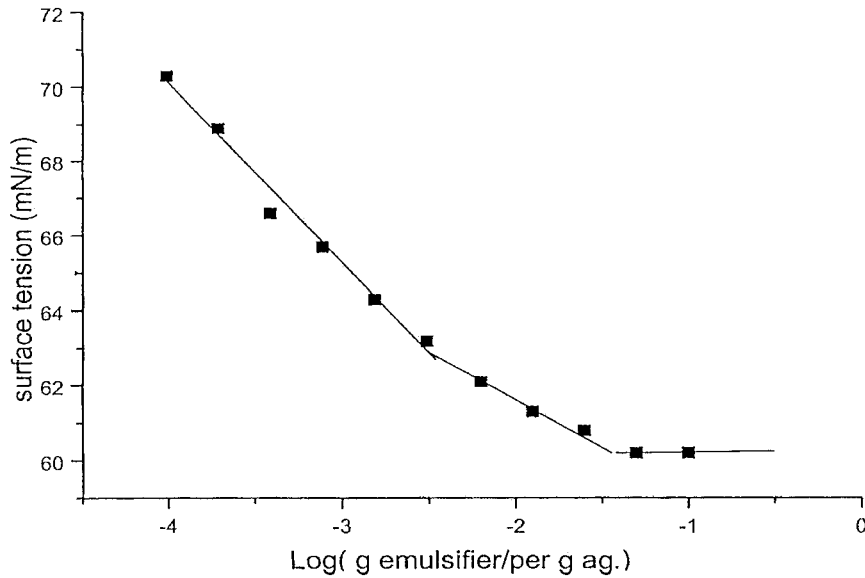
The SMTAPE emulsifier was A<sub>4</sub> SMTAPE emulsifier, the same as described by Chang and Lee,<sup>26</sup> and it was prepared by the condensation polymerization of diethylene glycol, isophthalic acid, and SSIPM. Its number-average molecular weight was 4700 g/mol with a molecular weight polydispersity around 2, and its acid number was 47.2. The amount of SSIPM incorporated was 10 mol % based on total diacid monomer.

### Emulsion Polymerizations

Emulsion polymerizations were performed in a 1-L, four-necked glass reactor equipped with a mechanical stirrer (a Teflon paddle stirrer), a reflux condenser, a thermometer, and a thermostated water bath for controlling the reaction temperature. A small flow of nitrogen was used to prevent oxygen from entering the reaction. The polymerizations were performed as follows. First, 410 g of deionized water, specific amounts of A<sub>4</sub> emulsifier, and potassium hydroxide were added to the reactor and then purged with nitrogen. The stirring speed controlled at 160 or 400 rpm. Next, the temperature was increased to 70°C, and after the emulsifier completely dissolved, the pH value was adjusted to 8.5 with the addition of a 1M potassium hydroxide aqueous solution. Then, 62.5 g of the styrene monomer was added. After 10 min, 0.62 g of potassium persulfate (dissolved in 15 g of deionized water) was added to start the reaction. Samples of known volumes were removed at given times with a hypodermic syringe. The samples were discharged in glass bottles containing two or three pieces of hydroquinone crystals and dropped in ice water to inhibit further polymerization. The total reaction was completed after 1.5 h.

### Analysis of the Particle Sizes

The particle sizes of SMTAPE micelles were determined with a Malvern 4700 dynamic light scattering spectrophotometer. The particle sizes



**Figure 1** Surface tension and cmc of  $A_4$  SMTAPE emulsifier in an aqueous solution.

of the polystyrene (PS) latices were determined by quasi-elastic light scattering with a Coulter Nano-sizer™.

#### Measurement of the Surface Tensions

The surface tensions of PS latices were determined with a CSC-DuNouy tensiometer at 25°C and 1 atm.

#### Transmission Electron Microscopy (TEM)

The PS latex particles were examined with a Hitachi H600 transmission electron microscope. Staining was performed through the exposure of dried samples to ruthenium tetroxide vapor prepared from ruthenium III chloride hydrate dissolved in a hyperchloride (Chlorox) solution. The PS phase appears dark in the TEM micrographs.

## RESULTS AND DISCUSSION

#### Surface Characteristic of $A_4$ SMTAPE

The evolution of the surface tension with the concentration of the  $A_4$  SMTAPE emulsifier in an aqueous solution is shown in Figure 1. The  $A_4$  emulsifier is a surface-active emulsifier. In addition, the  $A_4$  emulsifier possesses two critical micelle concentration (cmc) break points along the curve, which is attributed to the broad molecular weight distribution of SMTAPE.<sup>27</sup> The first break point is the cmc of the highest molecular weight

portion; the second break point is the cmc of the lowest molecular weight portion. The surface tensions are around 62.5 mN/m for the first cmc and 60.0 mN/m for the second cmc at room temperature.

#### Characteristics of Using $A_4$ SMTAPE in PS Emulsion Polymerization

Table I summarizes the results of using the  $A_4$  emulsifier in the emulsion polymerization of styrene. The extremely high reaction rates of the early stage of the reaction, shown in Figure 2, illustrate that a significantly high number of stable latex particles are formed in the early stage of the polymerization. When the concentration of the  $A_4$  emulsifier was as low as 10 wt %, coagulum formed during polymerization, and the particle size of the subsequent latex increased, indicating that the 10 wt % emulsifier concentration was the minimum amount required to stabilize the PS latex. This is consistent with the final surface tension of latex, being almost the same as the surface tension of the deionized water used in this experiment, and it shows that essentially all of the emulsifiers were adsorbed on the PS particle surface at the 10 wt % emulsifier concentration. The surface tension of the final latices with 20 wt % and 30 wt %  $A_4$  emulsifier exhibited surface tensions greater than 69 mN/m, which is also close to the surface tension of deionized water and shows that the  $A_4$  emulsifier anchored strongly onto the surfaces of the latex particles. Latices

**Table I** Subsequent Latex of Using A<sub>4</sub> SMTAPE Emulsifier on Emulsion Polymerization of PS Latices

Characteristic	Emulsifier Concentration (wt %) (Sample Number) <sup>a</sup>		
	10 ( <i>a</i> <sub>1</sub> )	20 ( <i>a</i> <sub>2</sub> )	30 ( <i>a</i> <sub>3</sub> )
Number of micelles × 10 <sup>16</sup> (per cm <sup>3</sup> ) <sup>b</sup>	2.3	4.6	8.6
<i>R<sub>p</sub></i> (max) × 10 <sup>-3</sup> (mol L <sup>-1</sup> s <sup>-1</sup> )	1.6	2.1	2.6
Coagulum (wt %)	0.8	< 0.2	< 0.2
Particle Size (nm)	54.6	49.4	47.2
Number of Particles × 10 <sup>15</sup> (per cm <sup>3</sup> ) <sup>c</sup>	1.4	1.9	2.2
Number of micelles particle/number of latex particles	16.4	24.2	39.1
Surface tension (mN/m) <sup>c</sup>	74.1	72.4	69.6

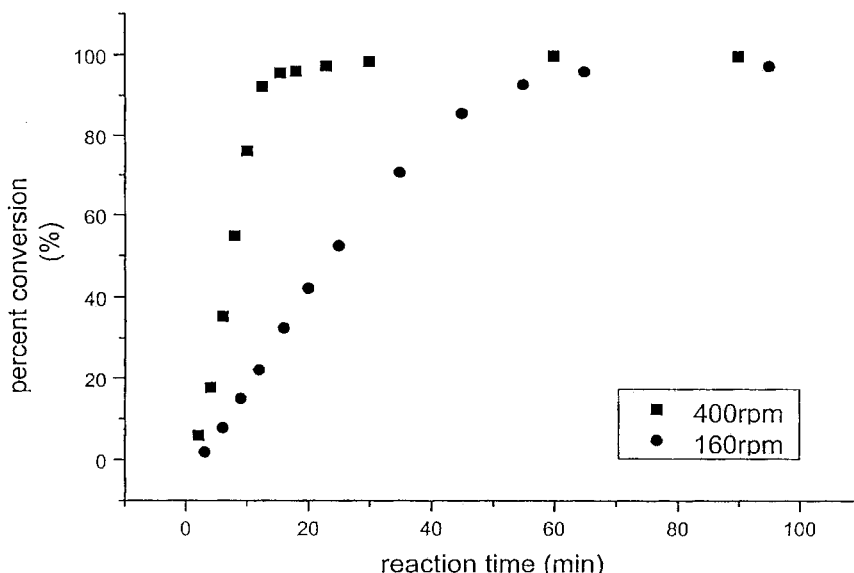
<sup>a</sup> Based on styrene monomer.<sup>b</sup> Per cm<sup>3</sup> emulsifier aqueous solution before reaction.<sup>c</sup> At full conversion.

produced with 20 % and 30% SMTAPE exhibited very low coagulum and good mechanical stability.

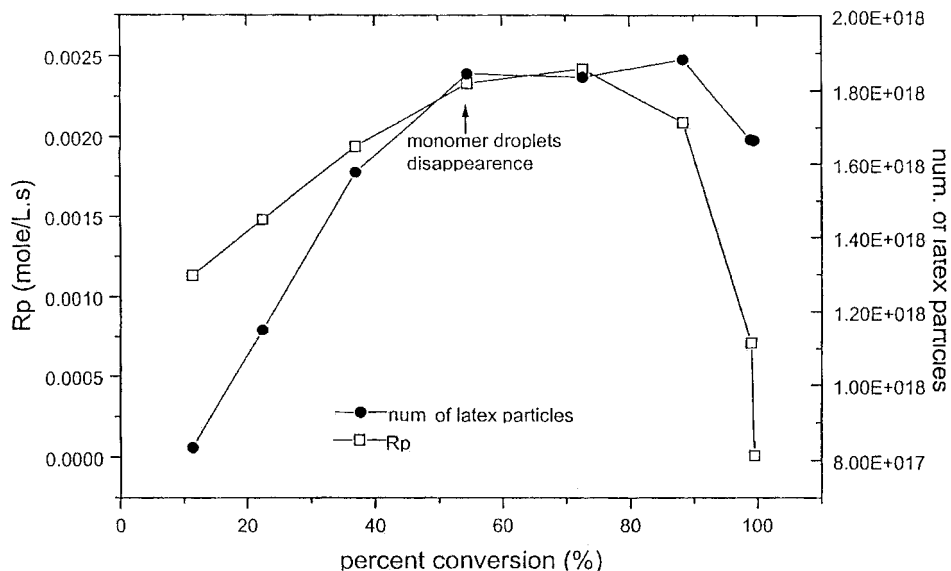
The stirring speed within the normal ranges used for latex reactions in the laboratory affected the kinetics. Figure 2 shows the effect of changing the stirring speed from 160 to 400 rpm on the reaction rate. The monomer pool surrounding the stirrer shaft was observed for a low stirring speed, and we believe it accounted for the slower reaction because the diffusion rate of the monomer to the particles was limited. Consequently, all of the other data reported in this article were obtained at a higher stirring speed.

### Nucleation During Reaction

The nucleation period extended to about 55% conversion, as shown in Figure 3, which is almost the same as the conversion of monomer-droplet disappearance and the conversion at the cmc, as shown in Figure 4. Such a long nucleation period is different with respect to conventional emulsion polymerization, in which nucleation ceases at about 15% conversion. At the initial stage of the reaction, the extremely high reaction rate illustrates that the radicals generated in the aqueous phase mainly enter the monomer-swollen mi-



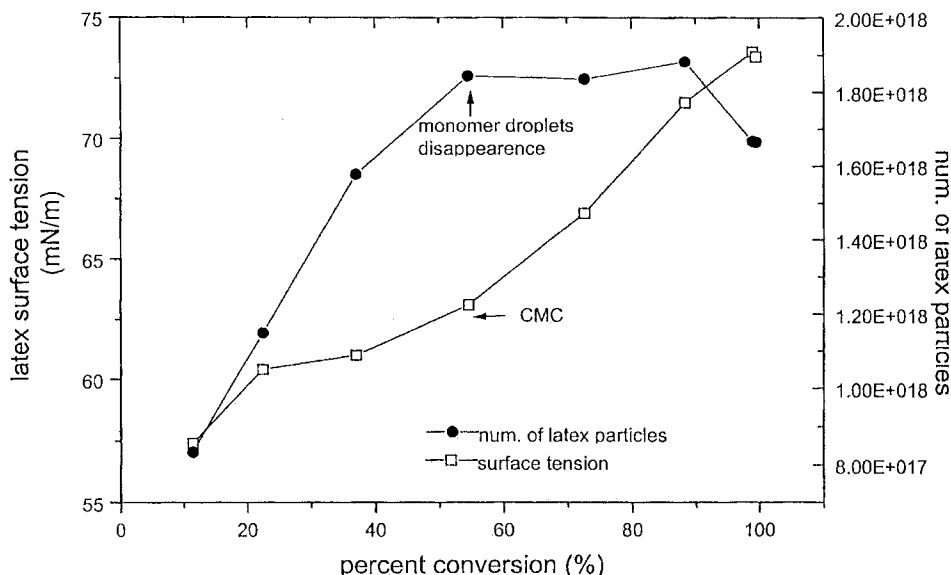
**Figure 2** Conversion versus time for different stirring speeds (with the same composition as *a*<sub>2</sub> in Table I).



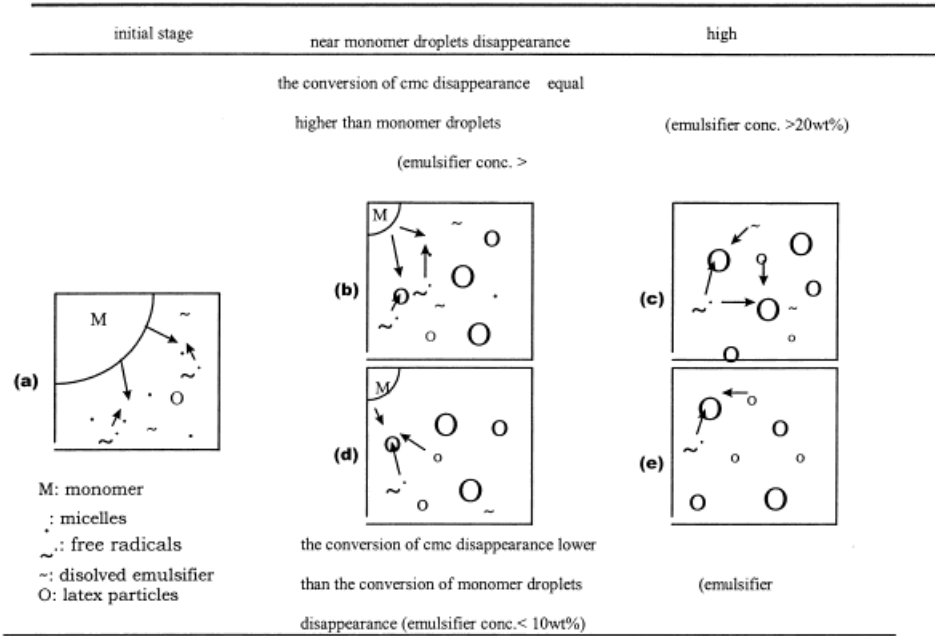
**Figure 3** Variation of  $R_p$  and number of latex particles with conversion during emulsion polymerization.

celles, and the monomer starts to polymerize, becoming a polymer particle as described in Figure 5(a). As the conversion is near the cmc, the number and total surface area of the micelles become smaller; in the meantime, the surface area of the polymer particles increase. Thus, the polymer particles increasingly compete with the micelles in capturing radicals, so the nucleation rate decreases, as shown in Figure 5(b) for the reaction

near the monomer-droplet disappearance for an emulsifier concentration greater than 20 wt %. Finally, nucleation ceases at the cmc or the monomer-droplet disappearance. The particle sizes increase to a conversion of about 55%, as shown in Figure 6, where we find the same conversion as for the monomer-droplet disappearance. During the nucleation period, the reaction rate increases with the increasing particles number. In this sys-



**Figure 4** Surface tension and number of latex particles as a function of conversion during emulsion polymerization.



**Figure 5** Nucleation mechanism for SMTAPE emulsifier in the emulsion polymerization of styrene.

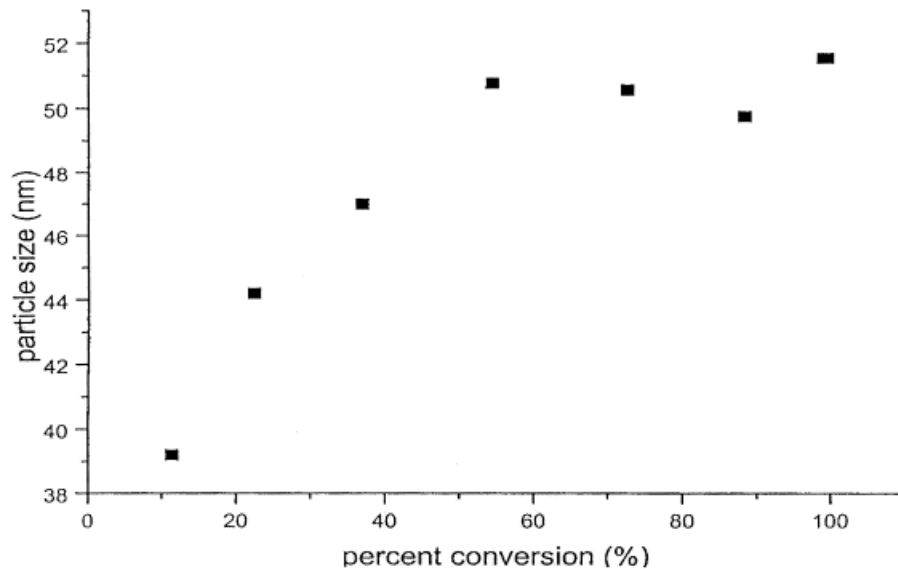
tem, no obvious Smith–Ewart interval II can be observed, as illustrated in Figure 3.

**Surface Tension During Polymerization**

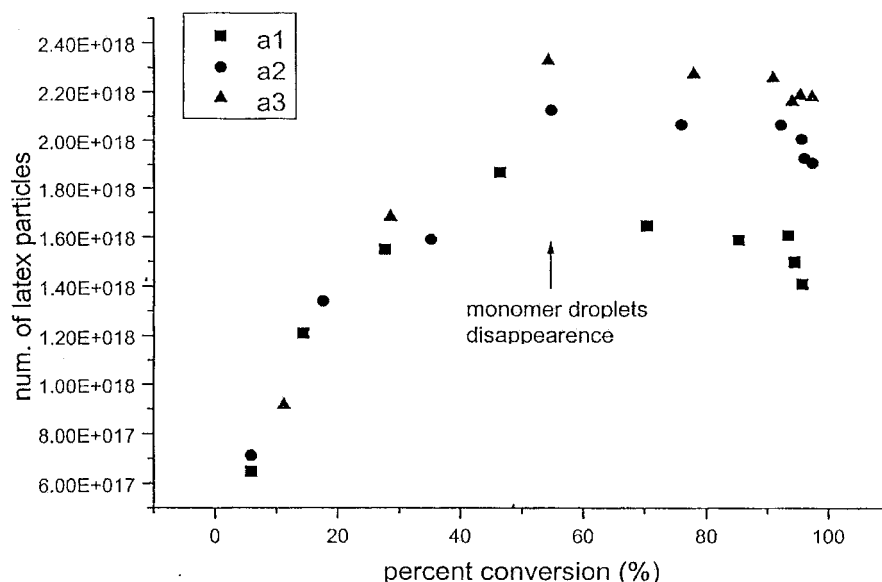
The consumption of the emulsifier during the reaction was determined by the monitoring of the surface tension of the latices. The amount of polymeric emulsifier or conventional emulsifier ad-

sorbed on a latex particle has been studied by the measurement of latex surface tension.<sup>6,29</sup> The initially low surface tension of the starting emulsion will increase in the course of the reaction because the emulsifier concentration is below the cmc.<sup>6</sup>

The concentration of A<sub>4</sub> emulsifier used in this study was 2.8 wt % in an aqueous solution (20 wt



**Figure 6** Particle size as a function of conversion during emulsion polymerization.



**Figure 7** Number of latex particles versus conversion for various SMTAPE emulsifier concentrations.

% based on the monomer), which is slightly lower than its second cmc. If styrene phase-separated from the samples in the early stage of polymerization, the measurements of surface tensions were performed for the aqueous phase of these samples.

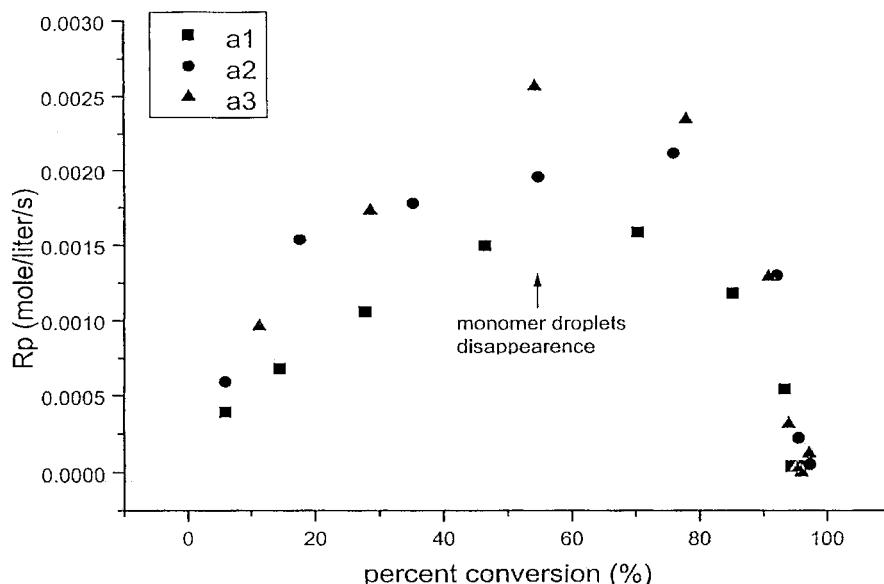
Figure 4 shows the surface tension of the latex rises with conversion. In a comparison with Figure 1, we find that after the first cmc, the rising rate increases and finishes at rather high levels. This is in contrast to traditional emulsion polymerization, for which the final surface tension is often about 50–60 mN/m when low molecular weight anionic surfactants are used.<sup>6</sup> Figure 4 also shows that the particle nucleation ceased at conversion around the cmc.

The emulsifier molecules in an aqueous solution continuously adsorb on latex particles as illustrated in Figure 5(c) for a high conversion. After the cmc, the surface tension still increases with increasing conversion. Because the monomer in the particle polymerizes continuously, this changes the surface property of the latex particle, so the emulsifier diffuses continuously into the particle surface to stabilize the particle. At a high conversion, the decrease in the particle number is probably caused by the exhaustion of the emulsifier, where the latex particles coagulate to reduce their surface area.

#### Effect of the SMTAPE Concentration

As in the traditional emulsion polymerization, an increase in the SMTAPE ( $A_4$  emulsifier) concentration will increase the number of micelles and the reaction rate but produce lower coagulum and smaller latex particle size, as shown in Table I. In addition, all of the reactions have a long Smith–Ewart interval I, and no interval II can be observed; the long interval I is also extended near the conversion of the monomer-droplet disappearance, as shown in Figures 7 and 8. At a high conversion, the particle number of latices for emulsifier concentrations greater than 20 wt % decrease slightly, which illustrates a possible effect of coagulation. When the emulsifier concentration is as low as 10 wt %, the end of the nucleation period seems to occur before the monomer-droplet disappearance, and then the particle number apparently decreases. This phenomenon implies that in 10 wt % emulsifiers, the nucleation period ceases at the cmc, and then coagulation occurs that is caused by unstable growing particles in which the monomer is supplied continuously from the monomer droplets, as described in Figure 5(d). At a high conversion, latex particles will coagulate slightly until the end of reaction, as shown in Figure 5(e).

The variation of  $\log[N_p]$  versus  $\log[S]$  is shown in Figure 9. This figure illustrates an exponent of



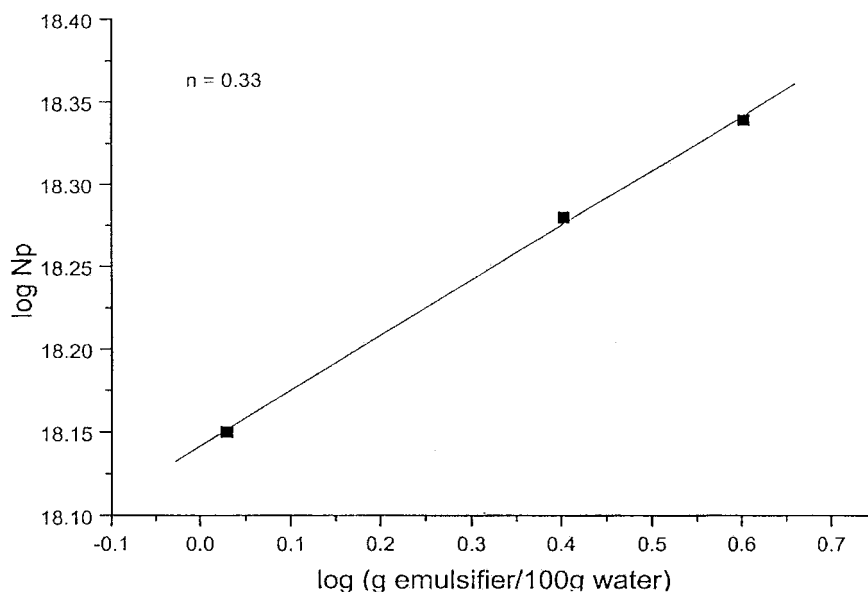
**Figure 8**  $R_p$  versus conversion for various SMTAPE emulsifier concentrations.

0.33 in the reaction, which is lower than the 0.6 power described in Smith–Ewart theory. This happens because coagulation occurs in this system, which is in contrast to the assumption of Smith–Ewart theory that no coagulation occurs during the emulsion polymerization.

Before the monomer-droplet disappearance,  $\bar{n}$  is between 0.17 and 0.34, and it is always less than 0.5, as seen in Figure 10. This is attributed to the chain transfer of growing polymers to the

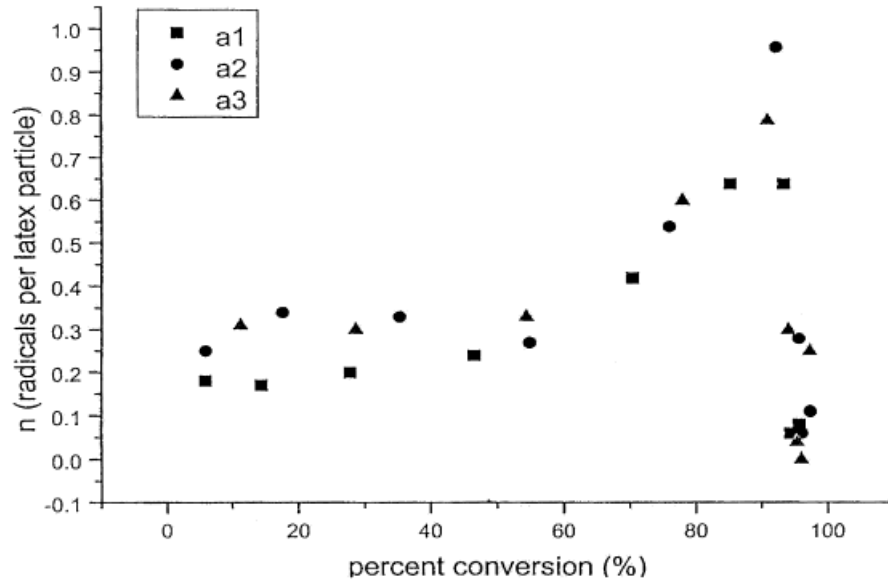
styrene monomer with the subsequent desorption of the newly formed monomer radicals.<sup>28</sup> After monomer droplets disappear, the particle size remained almost the same, but  $\bar{n}$  increases as the conversion increases. This agrees with the fact that a high viscosity inside particles at a high conversion decreases the diffusion-control termination rate.

Figure 11 shows that there is a broad particle size distribution throughout the reaction. A rela-



**Figure 9** Evolution of  $\bar{n}$  during emulsion polymerization in this system.





**Figure 10** Relationship of the particle number and the concentration of emulsifier in this system.

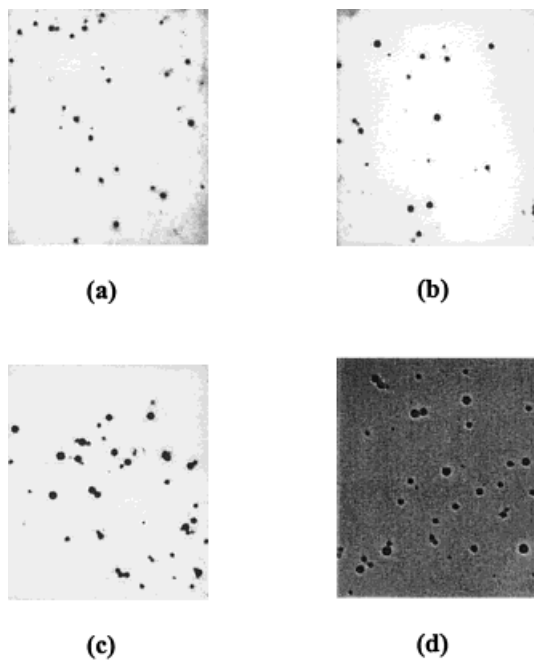
tively high particle size polydispersity was obtained in the particle size measurement via light scattering. These results strongly support a long nucleation period or a continuous nucleation mechanism in this system.

## CONCLUSIONS

The novel SMTAPE emulsifier provides a vast amount of micelles about 10 nm in size with a large surface area for emulsion polymerization, which leads to the conclusion that this reaction is a continuous micellar nucleation and does not exhibit Smith–Ewart interval II as the traditional reaction does. An observed broad particles distribution provides evidence of the continuous nucleation mechanism.

Kinetic analyses show that the nucleation rate is very fast at an early stage. The nucleation rate decreases when the conversion approaches the end of the particle nucleation period. Finally, the particle number decreases with coagulation. A relatively strong dependency of the nucleation periods on the amounts of micelles or the appearance of monomer droplets indicates that for the nucleation mechanism for a low emulsifier concentration ( $\leq 10$  wt %), the nucleation period lasts to the conversion of the cmc. For a high emulsifier concentration ( $\geq 20$  wt %), the nucleation period lasts to the conversion of the monomer-droplet disappearance.

An observed low value of  $\bar{n}$  is due to the small latex particle size in this reaction system causing a desorption of low molecular weight radicals that are generated by chain transfer to the monomer. The reaction rate increases with increasing  $\bar{n}$  after the monomer-droplet disappearance because



**Figure 11** TEM photography of the particle size distribution at different conversion: (a) 15%; (b) 50%; (c) 85%; (d) subsequent latex.

of a decrease in the diffusion termination rate of the high viscosity in the latex particles.

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