

# Kinetics of Emulsion Polymerization of Styrene Using the Reactive Surfactant HITENOL BC20

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**ABSTRACT:** The effect of the reactive surfactant HITENOL BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate; 20 U of ethylene oxide (EO)) on the emulsion polymerization of styrene was studied via reaction calorimetry (Mettler RC1; 70°C). For polymerizations carried out above the cmc of BC20, the reaction kinetics and evolution of the number of particles ( $N_p$ ) resembled those reported using the conventional surfactant sodium lauryl sulfate, indicating that nucleation proceeded by a combination of micellar and homogenous nucleation (Interval I and Stage 2). The reaction rate ( $R_p$ ) not only increased with increasing initiator ( $K_2S_2O_8$ ) and surfactant concentrations, as expected, but the increase in rate in Stage 2 was dependent on the initiator concentration and independent of the surfactant

concentration. This is consistent with the proposed nucleation mechanisms. The molecular weight increased with increasing surfactant concentration and decreasing initiator concentration as would also be expected for a conventional surfactant. The dependencies of  $R_p$  and  $N_p$  on the BC20 and initiator concentrations, however, were lower than the classical Smith-Ewart values ( $R_p \propto [E]^{0.47-0.52}$ ;  $R_p \propto [I]^{0.21-0.25}$ ) although  $R_p$  was found to be directly proportional to  $N_p$ . Chain transfer to the reactive surfactant is considered a likely source of divergence. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2275–2282, 2008

**Key words:** emulsion polymerization; styrene; reactive surfactant; kinetics

## INTRODUCTION

The use of reactive surfactants in emulsion polymerization has for some time been considered a promising means of alleviating some of the negative effects of conventional surfactants, which stem from their adsorption/desorption behavior.<sup>1</sup> These include latex particle instability under shear, latex foaming, and migration to pockets or interfaces during film formation increasing water-sensitivity and reducing adhesion and gloss. Recovery of the polymer via coagulation also requires measures to remove the desorbed surfactant from waste water. These deficiencies can potentially be largely reduced or eliminated by chemically incorporating the surfactant into the latex particles.

Although a reactive surfactant can take the form of an initiator (inisurf), chain transfer agent (transurf), or comonomer (surfmmer), it is the latter that is most favored in research and by manufacturers. In 1956 Bistline et al.<sup>2</sup> first obtained surface-active polymers referred to as surfmers. Since then, many anionic surfmers with sulfate or sulfonate head groups,

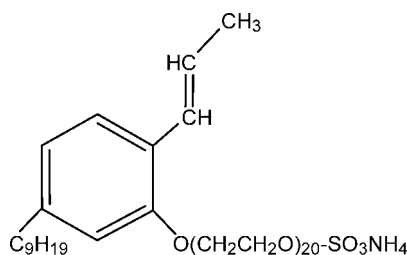
nonionic surfmers, and cationic surfmers have been synthesized and applied. Also, the synthesis of surfmers with various polymerizable groups, their copolymerization behavior, and their applications have been reported. Literature reviews on polymerizable surfactants have been written by Holmberg,<sup>3</sup> and more recently by Asua and Schoonbrood,<sup>1</sup> Guyot,<sup>4,5</sup> and Tauer.<sup>6</sup>

Some guidelines have been presented in the preceding reviews describing the qualities and characteristics sought in a good reactive surfactant. First, they should behave in a manner similar to conventional surfactants during an emulsion polymerization process in terms of providing emulsification of the monomer droplets, nucleation of polymer particles, and stabilization of these particles.<sup>1</sup> Second, by the end of the reaction, the surfactant should be incorporated into the copolymer and be present only on the surface of the resulting latex particles. Because of this requirement, some have proposed that the process of incorporation (by copolymerization) should be delayed to the end of the polymerization (e.g., Interval III in a batch reaction) so that none of the surfactant becomes buried inside the particles where it is wasted.

In this article, the reactive surfactant HITENOL BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate with 20 U of ethylene oxide) was used in emulsion polymerizations of styrene. The structure

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**Scheme 1** Chemical structure of the reactive surfactant HITENOL BC20.

is reproduced in Scheme 1. The reaction kinetics was studied using a Mettler RC1 reaction calorimeter with the intent of determining whether or not the kinetics are affected by the copolymerization of styrene with the reactive surfactant or by chain transfer reactions, which are considered likely owing to the presence of the ethylene oxide (EO) chain in the surfactant.

## EXPERIMENTAL

### Materials

HITENOL BC20 (polyoxyethylene alkylphenyl ether ammonium sulfate) anionic reactive surfactant (Daiichi Kogyo Seiyaku of Japan, manufacturer; Montello, distributor) was used as received. Styrene monomer (Sigma-Aldrich, St. Louis, MO) was repeatedly washed with 10% aqueous NaOH (Sigma-Aldrich) followed by deionized (DI) water and then dried over anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ , Fisher Scientific, Pittsburgh, PA). The styrene was then distilled at 45°C under reduced pressure (15 mmHg). Sodium bicarbonate ( $\text{NaHCO}_3$ ; Sigma-Aldrich), hydroquinone (Sigma-Aldrich) and potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ; Sigma-Aldrich) were used as received. THF (Sigma-Aldrich) was used as solvent in GPC measurements. All polymerizations were carried out using DI water.

### Polymerizations

Emulsion polymerizations were carried out in the 1 L MP10 reaction vessel of the Mettler RC1 reaction calorimeter equipped with a pitched blade impeller

and baffle. First, the surfactants and the buffer (sodium bicarbonate) were dissolved in DI water and charged into the MP10. The styrene was then added. Nitrogen was passed through the reactor for 10 min while stirring at 100 rpm; the nitrogen was turned off, the reactor was sealed, and the agitation rate was increased to 400 rpm. A first calibration was performed at 25°C to determine the heat transfer coefficient through the wall of the reactor. The reactor temperature was then ramped to 70°C over 10 min, and a second calibration was performed. The initiator, dissolved in 5 mL of DI water, was then injected through a septum. During the reaction, samples (3 or 10 mL) were withdrawn at regular intervals from the reactor. At the end of the reaction, 10 mL of a 1 wt % aqueous solution of hydroquinone was added to the reactor to short stop any further polymerization and a final calibration was then performed. The final conversion was determined gravimetrically. The heat of reaction ( $Q_r$ ) versus time was determined by evaluation of the data acquired during the reaction.

Typical recipes for polymerizations carried out in the RC1 reactor are shown in Table I. The reaction temperature was 70°C, and the final solids contents were 30 and 10 wt % for reactions above and below the cmc, respectively.

### Characterization

Samples withdrawn periodically from the reactor were analyzed in terms of conversion, particle size, and molecular weight. The monomer conversion was determined gravimetrically with some samples being confirmed by gas chromatography (GC, Hewlett-Packard 5890A). Capillary hydrodynamic fractionation (CHDF) (Matec Applied Sciences, Model 1100) was used to measure the particle size distributions (PSD) from which the particle size statistics were calculated. The number of particles ( $N_p$ ,  $\text{dm}^{-3}$  water) was estimated from the volume-average diameter and percent conversion.

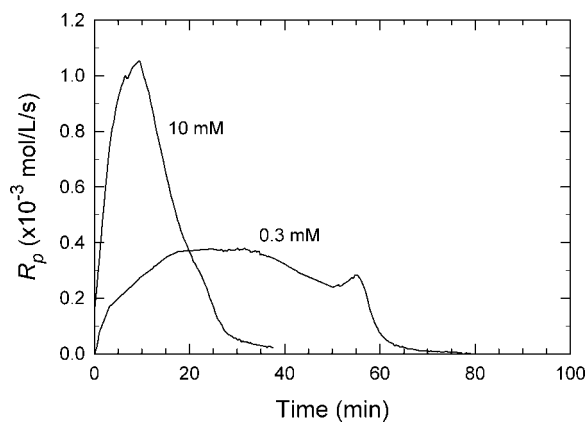
The molecular weight distribution (MWD) of the latex polymers was measured by gel permeation chromatography (GPC, Waters 515 HPLC pump/Waters 410 differential refractometer) using Micro-

**TABLE I**  
Recipes for the Emulsion Polymerization of Styrene with HITENOL BC20 Using the Mettler RC1 Reaction Calorimeter ( $T_r = 70^\circ\text{C}$ , 400 rpm)

Ingredient	Weight (g)	Concentration	Weight (g)	Concentration
Styrene	180	30 wt % solids	60	10 wt % solids
HITENOL BC20	5.393	3.00 % <sup>a</sup> (10 mM <sup>b</sup> )	0.208	0.35 % <sup>a</sup> (0.3 mM <sup>b</sup> )
DI water	420	30 wt % solids	540	10 wt % solids
$\text{K}_2\text{S}_2\text{O}_8$	0.113–0.454	1.0–4.0 mM <sup>b</sup>	0.113–0.454	1.0–4.0 mM <sup>b</sup>
$\text{NaHCO}_3$	0.141	4.0 mM <sup>b</sup>	0.141	4.0 mM <sup>b</sup>

<sup>a</sup> Based on styrene.

<sup>b</sup> Based on water phase.



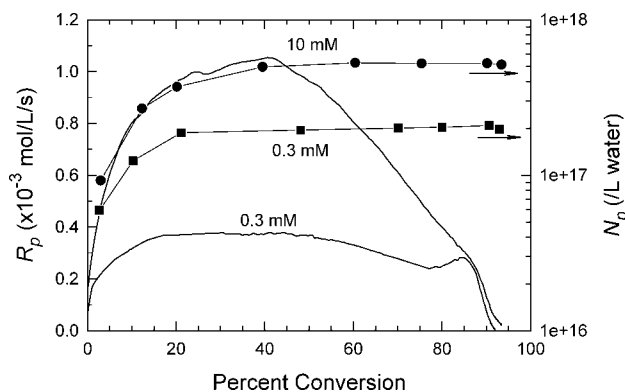
**Figure 1** Reaction rate as a function of reaction time for the emulsion polymerizations of styrene using 0.3 and 10 mM HITENOL BC20 concentrations; 1 mM KPS, 4 mM NaHCO<sub>3</sub> at 70°C, 400 rpm, 10 wt % solids content.

styrigel columns (MW 500–30, 5–600, 200–10,000K), from which the number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and polydispersity index (PDI) were obtained.

## RESULTS AND DISCUSSION

### Emulsion polymerization of styrene using HITENOL BC20 above and below the cmc

To understand the kinetics and mechanism of emulsion polymerization of styrene using HITENOL BC20, polymerizations were conducted with surfactant concentrations both above and below the cmc (0.80 mM). Initially, the reaction at 0.3 mM HITENOL BC20 was carried out at 30% final solids but ended with the formation of a substantial amount of coagulum (12%). Therefore, to compare above and below the cmc reactions, the solids content was reduced to 10%. Figure 1 shows the rates of reaction versus time while Figure 2 shows the evolution of the rate and number of particles with conversion. The final particle sizes ( $D_n$ ) were 70 and 93 nm for above and below the cmc, respectively. For the reaction at 10 mM surfactant, the kinetics shows an increase in rate to a maximum at about 40% conversion; no constant rate is seen and by examining Figure 1, Stage 2 (increasing rate and continued particle formation via homogeneous nucleation) also appears to be largely absent. This result is similar to that reported by Varela de la Rosa et al.<sup>7</sup> for the emulsion polymerization of styrene at 10% solids and 40 mM sodium lauryl sulfate (cmc = 6.2 mM). In these cases, the disappearance of micelles occurs in the neighborhood of the rate maximum where monomer droplets also disappear. This is the end of the nucleation stage, which in this case is primarily if not exclusively by micellar nucleation. Thus, Stage 2 (or Interval II) kinetics cannot be observed.

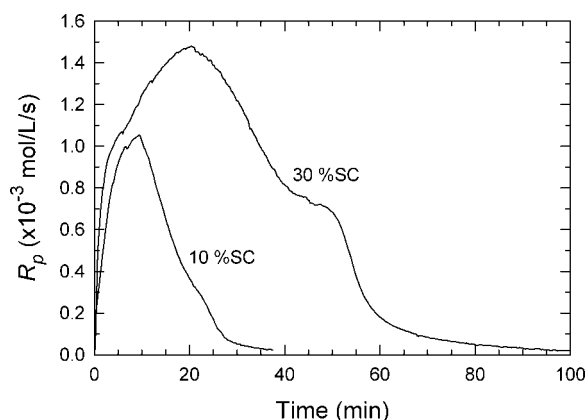


**Figure 2** Evolution of rate of polymerization and number of particles as a function of conversion in emulsion polymerizations of styrene using 0.3 and 10 mM HITENOL BC20 concentrations; 1 mM KPS, 4 mM NaHCO<sub>3</sub> at 70°C, 400 rpm, 10 wt % solids content.

For the reaction carried out below the cmc, the kinetics appear to fit the classical qualitative description of the emulsion polymerization process proposed by Harkins.<sup>8</sup> Interval I (particle nucleation) and Interval II (constant rate period; particle growth in the presence of droplets) are well defined, while an increase in rate owing to the gel effect appears in Interval III. Particle nucleation appears to be largely completed when a constant rate is achieved. The above results are quite similar to those reported for the conventional surfactant SLS<sup>9</sup> as well as the reactive surfactant TREM LF40 (sodium dodecyl allyl sulfosuccinate).<sup>10</sup>

### Effect of solids content

A comparison of the kinetics of the emulsion polymerization of styrene using 10 mM BC20 as surfactant (1.0 mM KPS and 4.0 mM NaHCO<sub>3</sub>) at 10 and 30 wt % final solids contents is shown in Figure 3. The rates of polymerization are similar up to about



**Figure 3** Comparison of the kinetics of the emulsion polymerization of styrene using 10 mM HITENOL BC20 as surfactant and 1 mM KPS as initiator at different solids contents at 70°C, 400 rpm, 4 mM NaHCO<sub>3</sub>.

**TABLE II**  
**Final Particle Size and Number of Polystyrene Latexes Prepared with 10 mM BC20 as Surfactant at Different Solids Contents**

Solids content (wt %)	Time (min)	X (%) <sup>a</sup>	Particle size (nm) <sup>b</sup>			$N_p$ ( $\times 10^{-17}$ dm <sup>-3</sup> water)
			$D_n$	$D_v$	PDI	
10	38	93.4	69.6	71.4	1.066	5.13
30	107	96.6	98.2	99.2	1.033	7.63

<sup>a</sup> By gravimetry.

<sup>b</sup> By CHDF.

5–10 min where the end of Interval I is indicated by the obvious change in slope of the 30% solids reaction. As described above, this is taken to be the end of micellar nucleation at which point similar numbers of particles should be formed. At the higher solids, the rate continues to rise at a more moderate rate and this is considered to be by Stage 2 nucleation of particles. Particle nucleation ends near the rate maximum (corresponding to the disappearance of monomer droplets) and thus a greater number of particles was produced at the higher solids as reported in Table II. These results imply that about  $2.5 \times 10^{17}$  particles/L or 33% of the total number

were nucleated in Stage 2 by homogeneous nucleation. This is consistent with a similar difference in the maximum rates observed in Figure 3.

#### Effects of surfactant and initiator concentrations

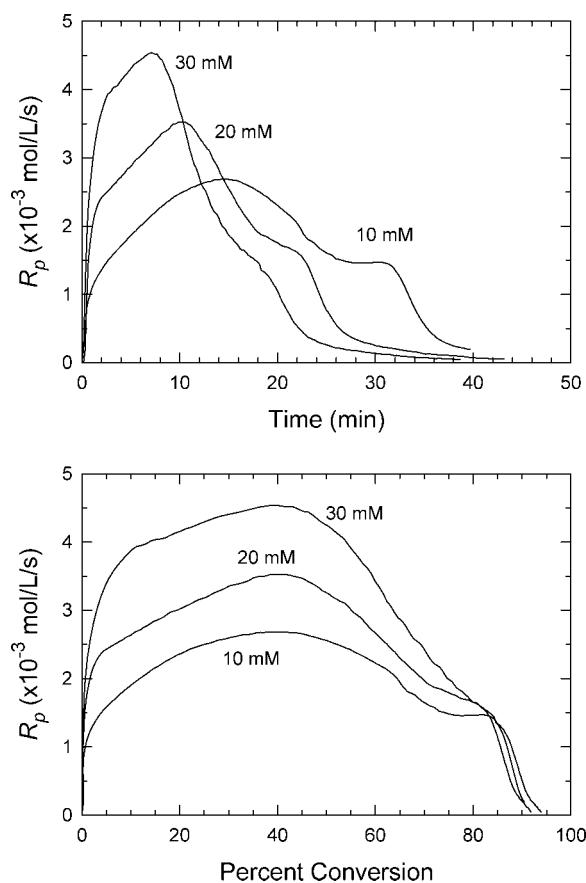
The BC20 surfactant concentration was varied (10, 20, 30 mM) and the kinetics of the emulsion polymerization of styrene measured as shown in Figure 4 as a function of (a) reaction time and (b) conversion. The reaction rate profiles follow those described earlier for Interval I, Stage 2, and Interval III kinetics.<sup>7</sup> As expected, the reaction rate increased with increasing surfactant concentration as for conventional surfactants, such as SLS.<sup>9</sup> The maximum reaction rate ( $R_{pmax}$ ) was reached at about the same conversion ( $\sim 40$  wt %) in all three systems. An increasing final number of particles with surfactant concentration is reported in Table III. Similar results were reported for the reactive surfactant TREM LF-40.<sup>10</sup>

Figure 5 shows the evolution of the number of particles as a function of reaction time and conversion for the polymerization using 10 mM BC20 and 4.0 mM KPS. It can be observed that after micelle disappearance, the number of particles still increased during Stage 2 through homogeneous nucleation. And during Interval III, the number of particles is approximately constant. The particle size statistics for all the reactions are reported in Table III. As expected, the number of particles increased with increasing surfactant concentration, and the particle size decreased.

As indicated in Table III, the initiator concentration was also varied (2, 4, and 8 mM KPS) within the surfactant series. Polymerization kinetics are reported in Figure 6 for 10 mM BC20 (similar results were seen at 20 and 30 mM BC20). As expected, the rate of polymerization increased with the increasing initiator concentration and the particle size decreased ( $N_p$  increased). Further analysis of all the results reveals some similarities and differences from prior work.

#### Dependencies of $R_p$ and $N_p$ on the surfactant and initiator concentrations

The dependencies of  $R_p$  and  $N_p$  on the surfactant and initiator concentrations are summarized in Table IV.



**Figure 4** Effect of BC20 surfactant concentration on reaction rate in emulsion polymerizations of styrene as a function of (a) reaction time and (b) conversion; 4 mM KPS, 4.0 mM NaHCO<sub>3</sub> at 70°C; BC20 concentration: 10, 20, and 30 mM.

**TABLE III**  
**Comparison of the Final Polystyrene Latexes Prepared by Emulsion Polymerization of Styrene at Different Initiator and Surfactant Concentrations**

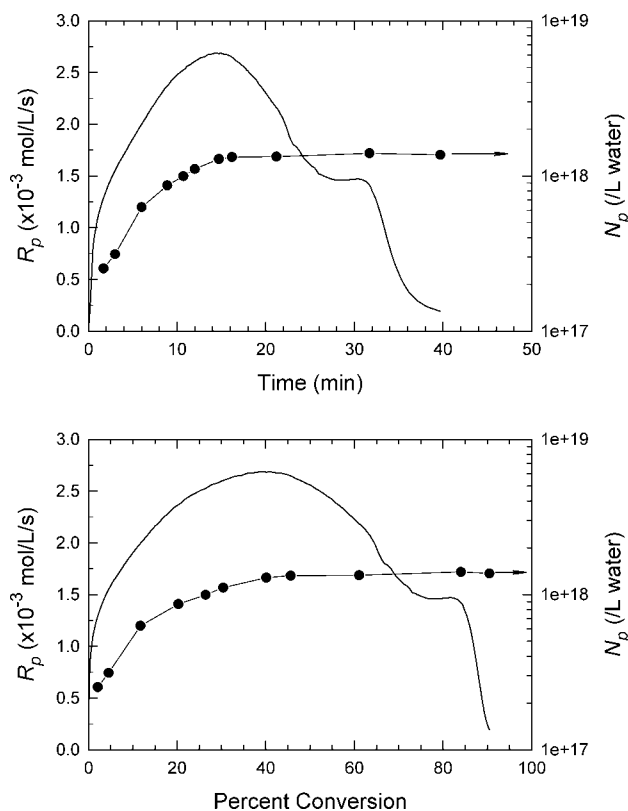
[BC20] (mM)	[KPS] (mM)	Time (min)	X (%) <sup>a</sup>	Particle size (nm) <sup>b</sup>				$R_p$ (max) ( $\times 10^3$ mol/dm <sup>3</sup> H <sub>2</sub> O/sec)	$N_p$ ( $\times 10^{-18}$ dm <sup>-3</sup> )
				$D_n$	$D_v$	$D_w$	PDI		
10	2	52	91.0	85.4	87.7	92.3	1.08	2.37	1.028
10	4	40	90.5	78.4	79.9	82.8	1.06	2.68	1.365
10	8	32.8	90.2	72.3	75.9	80.6	1.10	3.16	1.591
20	2	59	95.0	82.7	84.2	87.4	1.06	3.14	1.238
20	4	41.5	94.7	74.3	75.9	79.2	1.07	3.67	1.668
20	8	40.3	94.9	72.8	74.0	76.6	1.05	4.25	1.800
30	2	44.1	93.9	67.4	69.2	73.2	1.08	4.06	2.013
30	4	38.5	91.8	65.9	69.2	72.2	1.10	4.49	2.141
30	8	35.2	94.1	62.1	64.2	67.3	1.08	5.78	2.743

<sup>a</sup> By gravimetry.

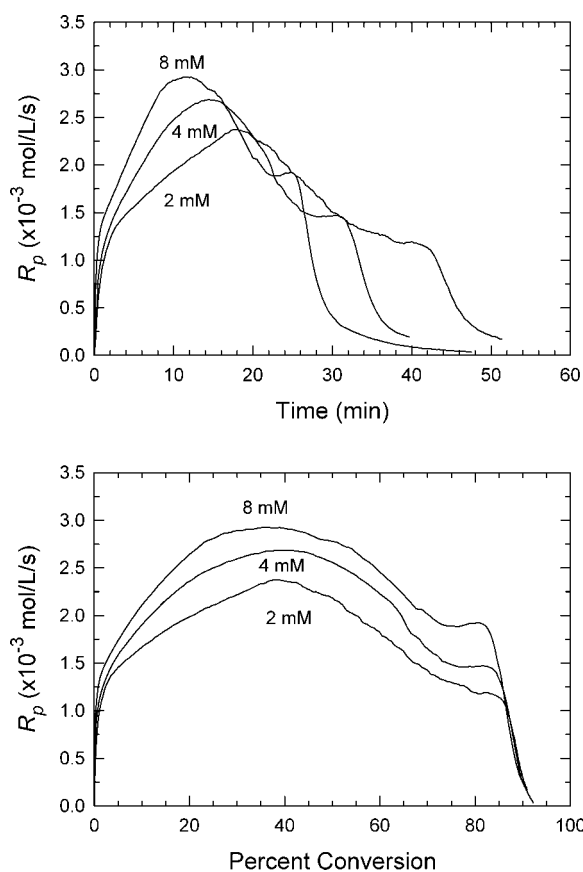
<sup>b</sup> By CHDF.

These are based on the maximum reaction rate and the final number of particles. One can see that  $R_p$  is directly proportional to the first power of the number of particles  $N_p$  as would be predicted by Smith-Ewart theory ( $R_p \propto N_p^{1.0}$ ).<sup>11</sup> This indicates that reactive surfactant Hitenol BC20 has qualitatively similar kinetic behavior as a conventional surfactant and differs from TREM LF-40 where  $R_p$  was found to be proportional to  $N_p$  to the 0.7 power under

conditions of varying surfactant concentration (20–40 mM TREM LF-40).<sup>12</sup> The latter was attributed to the combined effects of copolymerization, chain transfer, and reduced radical entry and exit rates owing to a “hairy” layer created by the TREM LF-40 incorporated into the surface of the polystyrene particles.



**Figure 5** Number of particles ( $N_p$ ) and reaction rate ( $R_p$ ) as a function of reaction time (a) and conversion (b) for the emulsion polymerization of styrene with 10 mM BC20, 4 mM KPS, 4.0 mM NaHCO<sub>3</sub> at 70°C.



**Figure 6** Effect of initiator (KPS) concentration on reaction rate of emulsion polymerization of styrene as a function of: (a) reaction time and (b) conversion; 10 mM BC20, 4.0 mM NaHCO<sub>3</sub> at 70°C; KPS: 2, 4, and 8 mM.

**TABLE IV**  
**Dependencies Obtained from the Kinetics of Emulsion Polymerization of Styrene Using BC20 as Surfactant, KPS as Initiator**

[BC20] (mM)	[KPS] (mM)	$R_p \propto [E]^A$ A	$N_p \propto [E]^B$ B	$R_p \propto N_p^C$ C
10–30	2	0.516	0.489	1.123
	4	0.466	0.423	1.028
	8	0.489	0.456	1.085
[BC20] (mM)	[KPS] (mM)	$R_p \propto [I]^A$ A	$N_p \propto [I]^B$ B	$R_p \propto N_p^C$ C
10 20 30	2–8	0.208	0.277	0.991
		0.219	0.209	0.995
		0.255	0.260	0.987

The results for BC20 do show some differences from a conventional surfactant such as SLS. Lower dependencies of  $R_p$  and  $N_p$  on both surfactant and initiator concentrations are seen:  $R_p \propto [E]^{0.47-0.52}$  (for 10–30 mM BC20),  $R_p \propto [I]^{0.21-0.26}$  (for 2–8 mM KPS). Differences from Smith-Ewart dependencies ( $R_p \propto [E]^{0.6}$  and  $R_p \propto [I]^{0.4}$ ), however, have been reported even for conventional surfactants.<sup>13–15</sup> Nonetheless, it is considered likely that the reactive surfactant plays some role in reducing these dependencies via copolymerization or chain transfer (to the EO groups).<sup>12,16</sup> Evidence for the latter was seen by comparing polymerizations using BC20 and its hydrogenated counterpart (i.e., no double bonds). It was concluded that during Interval I and Stage 2 about 25% of the BC20 became bound to the surface of the polymer particles via chain transfer while in Interval III the incorporation continued to about 90% via copolymerization. Complete characterization results are reported elsewhere.<sup>17</sup>

### Further analysis of stage 2

As already indicated, these results support the mechanism of emulsion polymerization put forth by Varela de la Rosa et al.<sup>7</sup> who proposed that particle nucleation continued in what was considered to be the region of Interval II in the classical description by Smith and Ewart. They termed this Stage 2 to distinguish it from Interval II where nucleation is considered to be complete and only particle growth takes place in the presence of monomer droplets. In Stage 2, nucleation continues by homogeneous nucleation and the rate of polymerization increases primarily because of the increase in  $N_p$ .

Examining the kinetics presented in Figures 4 and 6, one can see that the rate curves are consistent with the mechanism including Stage 2 nucleation; the number of particles increase in this stage as illustrated in Figure 5. Further examination reveals some important differences between the kinetics where the BC20 concentration (Fig. 4) and the KPS concentra-

tion (Fig. 6) are varied. First, note the point of transition between Interval I and Stage 2. In Figure 4 this transition takes place at higher values of  $R_p$  (and at longer times) while in Figure 6 the transition occurs at about the same  $R_p$  (and shorter times with increasing KPS). With increasing surfactant, more micelles are nucleated and it takes longer for them to disappear for the same radical production rate, while increasing the radical production rate has a relatively weak effect on the number of micelles nucleated at a given surfactant concentration.

Now note the slopes of the rate curves in Stage 2. In Figure 4(a) these are nearly independent of the BC20 concentration, while in Figures 6(a) they are strongly dependent on the initiator concentration. This could be understood as follows. In Figure 4(a), the transition to Stage 2 signifies the disappearance of micelles. In Stage 2 particle formation continues at a reduced rate by homogeneous nucleation. Since the same initiator concentration was used in all three cases, the radical production rate will be about the same at the transition and throughout Stage 2. Thus, similar numbers of particles are formed and the rates increase in nearly the same manner. Is this expected? Not completely since it might be expected that the rate of homogeneous nucleation should be affected by the number of particles formed in Interval I. Nonetheless, these are the findings. For a constant surfactant concentration and increasing KPS, Stage 2 takes place with increasing radical production rates and thus increasing amounts of homogeneous nucleation. This explains the greater slopes in Stage 2. In terms of the surfactant concentration, it should be clear that in all cases Stage 2 begins with basically the same concentration, just under the cmc of BC20.

### Molecular weights

The molecular weight averages for all samples are shown in Table V. We can see that the molecular weight increased with increasing BC20 surfactant concentration and decreasing KPS initiator concentration. This is what one normally expects for a conventional surfactant. The former effect is explained by the decreased radical entry rate per particle as more particles are produced with increasing surfactant. This result does not indicate that there are any significant chain transfer effects with BC20 during the emulsion polymerization. For TREM LF-40, Wang et al.,<sup>18</sup> reported that the molecular weight of the final latex decreased with increasing TREM LF-40, owing to chain transfer to TREM LF-40.

The dependencies of the molecular weight ( $M_n$ ) of the final latices on the initiator and surfactant concentrations are similar to those reported for  $R_p$  and  $N_p$  namely:  $M_n \propto [E]^{0.41-0.47}$  and  $M_n \propto [I]^{-0.23}$  to

TABLE V  
Molecular Weights of the Final Polystyrene Particles Prepared with varying BC20 and KPS Concentrations

[BC20] (mM)	[KPS] (mM)	Molecular weight (g/mol)				$N_p$ ( $\times 10^{-18} \text{ dm}^{-3}$ )
		$M_n$	$M_w$	$M_v$	PDI	
10	2	627,753	2,064,533	1,828,869	3.289	1.028
10	4	513,578	1,706,359	1,507,137	3.322	1.365
10	8	439,772	1,230,562	1,093,172	2.798	1.591
20	2	799,465	2,632,982	1,988,156	3.293	1.238
20	4	673,045	2,123,179	1,886,881	3.155	1.668
20	8	583,215	1,886,324	1,346,756	3.234	1.800
30	2	993,542	3,038,764	2,234,532	3.059	2.013
30	4	867,982	2,211,042	1,980,063	2.547	2.186
30	8	698,782	2,094,567	1,980,063	2.997	2.743

$-0.26$ . These are lower than reported for the conventional surfactant SLS as well.

The evolution of the molecular weight of the latex as function of conversion was also studied for several reactions. Figure 7 shows  $M_w$  as a function of conversion for the polymerization employing 10 mM BC20 and 2.0 mM KPS. The molecular weight increases with increasing conversion until the end of the reaction where a decrease is noted. The increase is linear up to about 45% conversion after which it appears that the increase slows and resumes again basically with the same slope up to about 85% conversion. Qualitatively these results can be understood as follows. During the nucleation (in this case Interval I and Stage 2) the number of particles increases and thus the radical entry rate per particle must decrease as the available radicals are shared by an increasing number of particles. Thus the molecular weight goes up. After nucleation ceases and droplets disappear, the radicals are shared with an unchanging number of particles and thus the molecular weight should increase little (some reduction in the rate of radical production occurs owing to the consumption of initiator). The gel effect begins, how-

ever, around 70% conversion, which also increases the molecular weight caused by a reduced termination rate. At 85% conversion the glass effect takes over slowing the reaction considerably (see rate of polymerization curve in Fig. 6). The reduced rate leads to a higher radical entry rate per amount of polymer produced, thus lowering the molecular weight.

## SUMMARY

The kinetics of emulsion polymerizations of styrene using the reactive surfactant Hitenol BC20 resemble reactions carried out with the conventional surfactant sodium dodecyl sulfate. The rate of polymerization increases with both surfactant and initiator concentrations. The rate of polymerization versus time (or conversion) profiles show Interval I, Stage 2, Interval III kinetics. Nucleation of particles occurs beyond Interval I (micellar nucleation) and thus Stage 2 (homogeneous nucleation) behavior is invoked. The dependencies of  $R_p$  and  $N_p$  on the BC20 and initiator concentrations are lower than the Smith-Ewart values of 0.6 and 0.4, respectively, although  $R_p$  is directly proportional to the first power of  $N_p$ . The molecular weight increases with increasing surfactant concentration and decreasing initiator concentration. These results indicate that the reactive surfactant HITENOL BC20 behaves much as a conventional surfactant during most of emulsion polymerization process in terms of its influence on the reaction kinetics.

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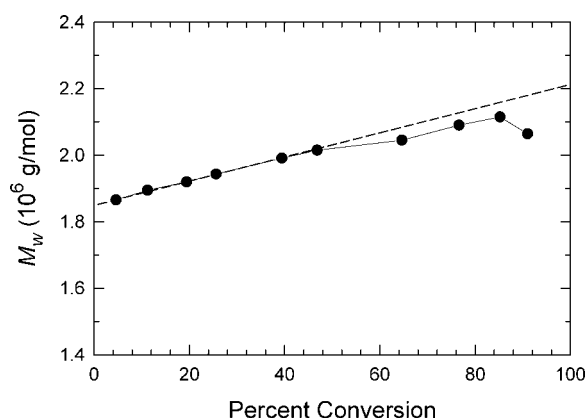


Figure 7 Evolution of the weight-average molecular weight for a styrene emulsion polymerization carried out with 10 mM BC20 and 2.0 mM KPS at 70°C, 400 rpm.

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