

## The stabilization effect of mixed-surfactants in the emulsion polymerization of *n*-butyl acrylate

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### SUMMARY

Using a blend of anionic and nonionic surfactants, the emulsion polymerization of *n*-butyl acrylate was conducted at 50°C. The total particle surface area per cm<sup>3</sup> of aqueous solution (TS) at 90% conversion was found to be proportional to the amount of surfactant (E) used in the single-surfactant systems. A relationship close to additive exists between the TS value and the E of each surfactant used. For most of the recipes, the latex particles were uniform throughout the polymerization. However, in some recipes, the particle number varied during the polymerization.

### INTRODUCTION

An effective way to prepare monodisperse latexes is to conduct emulsion polymerizations with a blend of anionic and nonionic surfactants (1). This has attracted a lot of attention. A series of experiments were carried out to investigate the stabilization effect of the mixed-surfactants in the emulsion polymerizations (2,3). Chu and Piirma (2) studied this effect for styrene, where a relationship between the mixed-surfactants and respective single-surfactants was found to be close to additive. A similar approach was found applicable to the system of methyl methacrylate (MMA) (3) but with different values in characteristic constants. The same approach can be applied to emulsion polymerization of other monomers and each system has its own characteristic constants. Therefore, this introduces a clearer idea for the stabilization of mixed-surfactants.

In this report, interest was placed on the system of *n*-butyl acrylate. Poly(*n*-butyl acrylate) (PBA) is a flexible polymer with a glass transition temperature of -56°C (4). Its good film-forming property made it popular in the coating industry, and it is mostly used as a component of copolymers. Limited data are available in the literature for the stabilization effect of mixed-surfactants in emulsion polymerization of *n*-butyl acrylate. Most reports for the emulsion polymerization of *n*-butyl acrylate are concerning either copolymerizations (5-7), or the use of single-surfactants (8). Therefore, an attempt was made to

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investigate the characteristic constants of n-butyl acrylate to further clarify the stabilization effect of mixed-surfactants.

## EXPERIMENTAL

### Materials

The n-butyl acrylate monomer (BA) was washed with aqueous sodium-hydroxide solution followed by doubly-distilled water, dried over anhydrous sodium sulfate, vacuum-distilled, and stored at 5°C until used. The non-ionic surfactant (Emulphogene BC-840,  $C_{13}H_{27}O(CH_2CH_2O)_{1.5}H$ ) was treated by heating at 70°C overnight under vacuum to destroy any peroxides. Water was doubly distilled. The anionic surfactant, sodium dodecyl sulfate (SDS) and others were used as received.

The general recipe is shown in Table 1. The initiator is  $K_2S_2O_8$  and the emulsifier is a mixture of Y gram of SDS and X grams of BC-840, where Y ranges from 0 to 0.90g and X ranges from 0 to 4.0g.

### Polymerization

Polymerizations were performed in 250 mL four-neck round bottom flasks at 50°C in a constant temperature water bath. The apparatus, conditions, and procedure are the same as those in Reference 3.

The particle size was determined with a Photal DLS-3000/3100 dynamic light scattering spectrophotometer (DLS). Some results were verified with a JOEL JEM-200CX transmission electron microscope (TEM). The formulas for the computation of the number-average diameter ( $D_n$ ), volume-average diameter ( $D_v$ ), and weight-average diameter ( $D_w$ ) can be found in Reference 2. The particle number (N) and total particle surface area (TS) per  $cm^3$  of aqueous phase are computed as follows:

$$N = 6(M/W) (\% \text{ Conversion}) d_w / [100\pi d_p (D_v)^3 (10^{-24})] \quad (1)$$

and

$$TS = 6(M/W) (\% \text{ Conversion}) d_w / [100 d_p D_v (10^{-24})] \quad (2)$$

where  $M/W$  = weight ratio of monomer to water in the recipe,  
 $d_w$  = density of water = 1.00  $g/cm^3$ ,  
 $d_p$  = density of PBA = 1.10  $g/cm^3$ ,  
 $D_v$  in (Å) and TS in (Å)<sup>3</sup>/ $cm^3$ .

Table 1  
Polymerization Recipe at 50°C

BA	37.5	g
water	165.0	g
$K_2S_2O_8$	0.188	g
SDS	variable	
BC-840	variable	

## RESULTS AND DISCUSSION

### Effect of the Amount of the Surfactants on Latex Particle Size

Data for the volume average particle diameter ( $D_v$ ) of different recipes at 90% conversion are shown in Table 2, where  $D_v$  is in between 820 and 1800 Å. This is quite different from the results of MMA (3) or styrene (2). In case of BA, the differences in  $D_v$  were found to be narrower between the data obtained from SDS and BC-840. The particle size distributions,  $D_w/D_n$ , are mostly below 1.10 as shown in Table 3. The narrow distribution indicates the stabilization effect of the blend of SDS and BC-840 on the PBA latex.

### Stabilization Effect of Mixed-Surfactants

In single-surfactant systems, the relationship between TS and E (i.e., amount of surfactant) is

$$TS = a E^b \quad (3)$$

where "a" is the intercept and "b" the slope of  $\log(TS)$  versus  $\log(E)$  plots. The values of "a" were  $1.26 \times 10^{21}$  and  $4.68 \times 10^{20}$  for SDS and BC-840, respectively; while those of "b" were 0.318 and 0.556 for SDS and BC-840, respectively. The results are shown in Figure 1. Unlike in the emulsion polymerization of MMA, the deviation in the value of "b" was not large between SDS and BC-840

Table 2  
Volume average particle diameters at approximately 90% conversion, (unit:Å)

Nonionic Surfactant, BC-840 (g)	Anionic Surfactant, SDS (g)				
	0	0.30	0.45	0.60	0.90
0	-	1350	1110	1160	1060
2.00	1730	1220	-	996	912
2.50	1400	-	-	-	-
3.00	1230	932	-	860	876
3.50	1220	-	-	-	-
4.00	1160	-	-	-	826

Table 3  
Effect of varying the surfactant composition on the polydispersity index

Nonionic Surfactant, BC-840 (g)	Anionic Surfactant, SDS (g)				
	0	0.30	0.45	0.60	0.90
0	-	1.02	1.22	1.03	1.21
2.00	1.04	1.07	-	1.03	1.05
2.50	1.08	-	-	-	-
3.00	1.06	1.10	-	1.04	1.04
3.50	1.02	-	-	-	-
4.00	1.02	-	-	-	1.04

in the case of BA. However, a difference in the intercept did exist. This reveals that SDS has a much higher stabilization efficiency than BC-840 when recipes with lower emulsifier concentrations are compared.

To scrutinize the existence of additivity between  $TS_m$  and  $(TS_i + TS_n)$ , the corresponding data are shown in Figure 2. The subscripts  $m$ ,  $i$ , and  $n$  refer to the mixed-surfactants, SDS, and BC-840, respectively.  $TS_n$  stands for data of  $X$  grams of BC-840,  $TS_i$  for  $Y$  gram of SDS, and  $TS_m$  for a blend with  $X$  grams of BC-840 and  $Y$  gram of SDS. The following relationship was obtained:

$$TS_m = c + d (TS_i + TS_n) \quad (4)$$

where "c" is the intercept and "d" is the slope.

Substituting Equations (2) and (3) into Equation (4) and using the values of the corresponding constants, we obtain:

$$[D_v]_m = (1.12 \times 10^{24}) / (-3.41 \times 10^{20} + 3.88 \times 10^{20} X^{0.556} + 1.04 \times 10^{21} Y^{0.318}) \quad (5)$$

The error between the predicted and the experimental values were calculated for Equation (5), as shown in Table 4.

Data for particle diameters determined by DLS and TEM are compared in Table 5. The average deviation is below 7%. However, it should be noted that only a limited number of latex samples have been examined by TEM under conditions that sufficient amounts of particles were counted. Therefore, these data may be inaccurate.

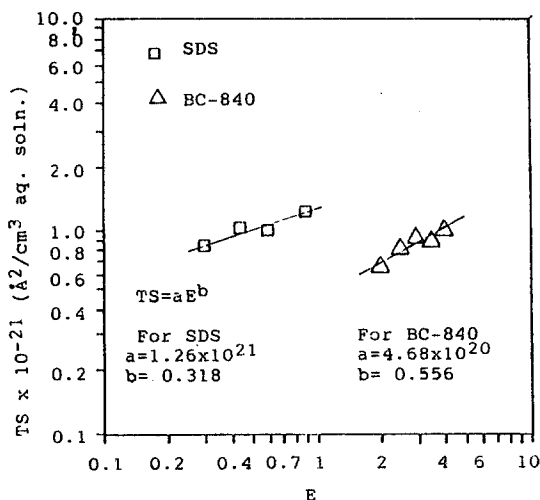


Fig. 1. Correlation between the total particle surface area per  $cm^3$  of aq. solution (TS) at 90% conversion and the amount of surfactant (E)

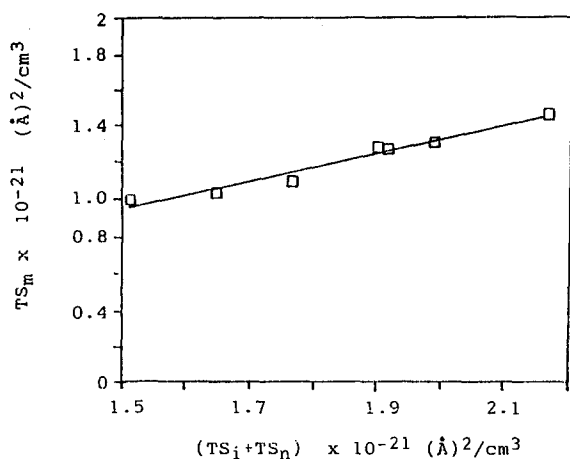


Fig. 2. Correlation between  $TS_m$  and  $(TS_n + TS_i)$

Table 4  
The errors between the predicted values of equation (5) and the experimental values, (unit : Å)

BC-840 (g)	SDS (g)	$D_v$ pred., Å	$D_v$ expt., Å	% Error
2.00	0.30	1190	1220	-2.46
2.00	0.60	1010	996	1.41
2.00	0.90	906	912	-0.66
3.00	0.30	1030	932	10.5
3.00	0.60	889	860	3.37
3.00	0.90	811	876	-7.42
4.00	0.90	744	826	-9.93
			Avg.	5.11

Two TEM pictures for PBA are shown in Figure 3. The particles tend to agglomerate and have a flattened appearance compared to those polystyrene latex particles that are usually seen. Agglomeration may be due to the fact that PBA has a higher solubility in water than PS. The flattened appearance may be related to the fact that PBA has a lower glass transition temperature and is a good film-former. The particles tend to be softened or swollen under the electron beams.

Moreover, the particle size determined in the aqueous phase is different from that in the dry state. Thus, the particle diameter determined by DLS, (but not by TEM) may be closer to the real particle size in the latex.

The stabilization effect of SDS/BC-840 mixture has been correlated for the emulsion polymerizations of styrene (2), MMA (3), and BA. Table 6 outlines these results. The characteristic constants reflect the nature of each system.

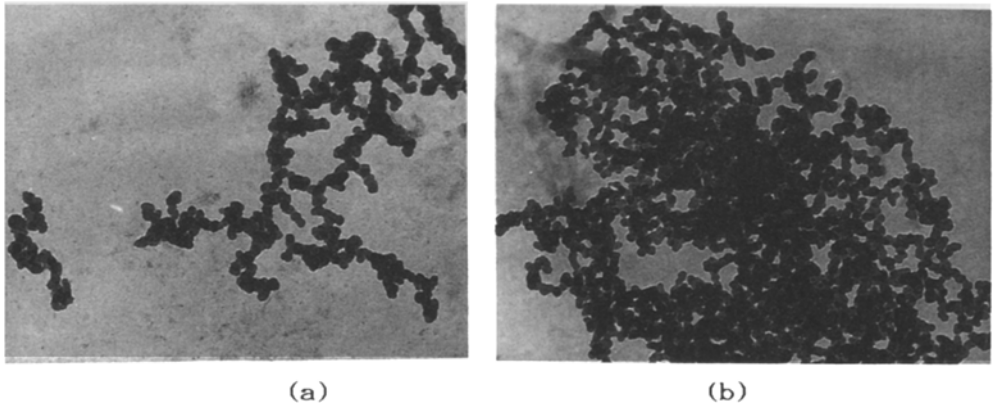


Fig. 3. TEM pictures of PBA latex particles

Table 5  
Comparison of particle size data obtained from TEM and DLS

BC-840 (g) % Conversion	TEM (nm)	DLS (nm)	% Error
2.00 g 92.7%	$D_v = 162$	$D_v = 173$	6.79
	$D_n = 169$	$D_n = 179$	5.92
	$D_w = 175$	$D_w = 172$	-1.71
	$D_w/D_n = 1.04$	$D_w/D_n = 1.04$	
3.00 g 90.5%	$D_v = 133$	$D_v = 123$	-7.52
	$D_n = 131$	$D_n = 121$	-7.63
	$D_w = 136$	$D_w = 122$	-10.3
	$D_w/D_n = 1.04$	$D_w/D_n = 1.01$	
4.00 g 91.5%	$D_v = 110$	$D_v = 114$	3.64
	$D_n = 109$	$D_n = 117$	7.34
	$D_w = 114$	$D_w = 113$	-0.88
	$D_w/D_n = 1.05$	$D_w/D_n = 1.03$	
Avg. % Error			$D_v = 5.98$
			$D_n = 6.96$
			$D_w = 4.30$

Table 6  
Characteristic constants "a" and "b" in Equation (3) and "c" and "d" in Equation (4) for each monomer system

Monomer	Emulsifier		
	SDS	BC-840	Mixed
styrene (2)	$a = 3.37 \times 10^{21}$ $b = 0.079$	$a = 3.79 \times 10^{20}$ $b = 1.00$	$c = -9.92 \times 10^{20}$ $d = 1.32$
MMA (3)	$a = 1.28 \times 10^{21}$ $b = 0.158$	$a = 5.54 \times 10^{19}$ $b = 2.95$	$c = 2.28 \times 10^{21}$ $d = 0.913$
BA	$a = 1.26 \times 10^{21}$ $b = 0.318$	$b = 4.68 \times 10^{20}$ $b = 0.556$	$c = -3.41 \times 10^{20}$ $d = 0.829$

### Variation of the Number of Particles During Emulsion Polymerization

Using blends of SDS and BC-840 at certain concentration levels, the emulsion polymerization of some monomers can yield uniform particles (2,3). However, it was found that new nucleations took place from time to time during the polymerization. Similar findings have been reported elsewhere (9-13), and fluctuations in particle numbers in the emulsion polymerizations for a variety of monomers have been observed.

The PBA latices exhibited low polydispersity and no obvious coagulation was observed by the naked-eye. In spite of this, we found particle number fluctuations during the course of the emulsion polymerization, as illustrated in Figures 4 and 5.

The corresponding results for  $D_w/D_n$  are shown in Figures 6 and 7. It is interesting to find that polydispersity values were below 1.20, even though fluctuations in particle number took place. Evidently the PBA latex has a short growth period or coagulates quickly once new nucleation occurred.

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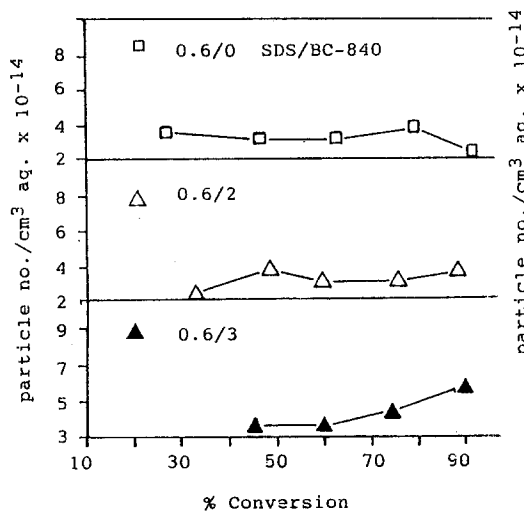


Fig. 4. The variation of particle number during the polymerization

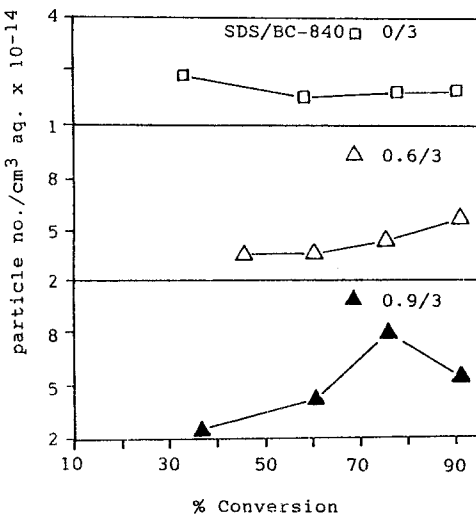


Fig. 5. The variation of particle number during the polymerization

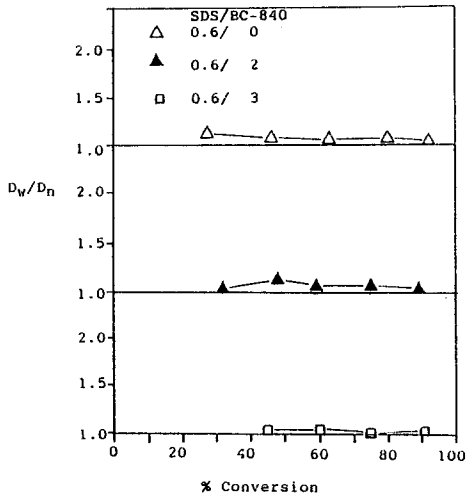


Fig. 6. The variation of polydispersity of the particle diameter during the polymerization

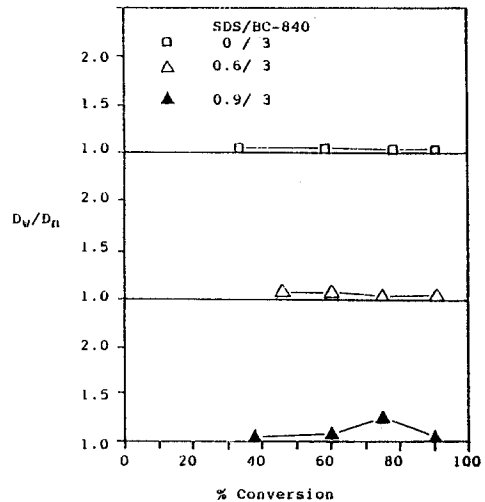


Fig. 7. The variation of polydispersity of the particle diameter during the polymerization

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