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The stabilization effect of mixed-surfactants in the emulsion polymerization of methyl methacrylate

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SUMMARY

The emulsion polymerization of methyl methacrylate (MMA) was conducted at 50℃ using either anionic or nonionic surfactants, or a mixture of the two at different surfactant concentrations. In the single-surfactant systems a proportional relationship was observed between the total particle surface area per cm^3 of aqueous solution at 90% conversion (TS) and the amount of surfactant used. For mixed-surfactant systems, a relationship close to an additive one was found between the TS value and the amount of each surfactant used. The particle number did not remain constant during the polymerization, while the TS value continuously increased. It was also found that MMA formed a paste easily at higher (M/W) ratios, which could be alleviated by using higher surfactant concentrations.

INTRODUCTION

Mixtures of anionic and nonionic surfactants have been found to produce monodisperse latices. This was reported by Woods et al. (1), where they prepared monodisperse latices at a solid content of 50% with a mixture of anionic and nonionic surfactants. Further studies (2-6) have been conducted to elucidate the synergistic effect of combinations of nonionic and anionic surfactants on latex stability.

Recently, Chu and Piirma (7) reported relationships betweeen TS and surfactant concentration for both single-surfactant and mixed-surfactant systems of styrene, where the former has a proportional relationship and the latter has an additive one. They also pointed out that the particle number changed with conversion.

In this study, interest was placed on the stabilization effect of mixed-surfactants in the emulsion polymerization of MMA. It is known that MMA has a much higher water-solubility than styrene and the aqueous phase polymerization becomes relatively important in the emulsion polymerization of MMA (8). Also, consideration should be focussed on the paste formation which occurs during the emulsion polymerization. The "sticky state" (9) may have an adverse effect on the particle stability, since polymer is dissolved in the monomer, thus increasing the viscosity of the disperse phase. All these factors may complicate the stabilization effect, and an effort was made to determine if the stabilization effect of mixed-surfactants seen using styrene also occurrs in the emulsion polymerization of MMA.

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EXPERIMENTAL

Materials

MMA was purified by prewashing and vacuum distillation. The nonionic surfactant (Emulphogene BC-840, $C_{13}H_{27}O(CH_2CH_2O)_{15}H$) was treated by heating at 70℃ overnight under vacuum to destroy any peroxides. Water was doubly distilled. All others were used as recived.

Polymerization Recipes

The general recipe is shown in Table 1. In each recipe, the initiator is $K_2S_2O_8$;and the emulsifier is a mixture of X grams of SDS (or sodium dodecyl sulfate, an anionic surfactant) and Y grams of BC-840, where X ranges from 0 to 0.90 g and Y ranges from 0 to 5.5 g.

Table 1
Polymerization Recipe at 50℃

MMA	37.5 g
Water	165.0 g
$K_2S_2O_8$	0.188 g
SDS	variable
BC-840	variable

Polymerization

Polymerizations were carried out in 250 ml four-neck round bottom flasks at 50℃ in a thermostatted water bath. The flask was equiped with a mechanical stirrer, a thermometer, a reflux condenser and a nitrogen inlet. After all of the components were charged into the flask, the stirring rate was set at 240 rpm for 5 minutes and then reduced to 120 rpm. Samples for monomer conversion and for particle size measurements were withdrawn using a hypodermic needle and a syringe. The conversion of monomer to polymer was determined gravimetrically.

Particle Size Analysis

The particle size was determined with a Photal DLS-700 dynamic light scattering spectrophotometer. The particle sizes of some samples were double-checked with a JOEL JEM-200CX Transmission Electron Microscope (TEM). The computation of the number-average diameter (D_n), volume-average diameter (D_v), weight-average diameter(D_w), and the number of particles per cm^3 of aq. solution (N) followed the same formulas as were shown in Reference (7). The TS value was computed as follows:

$$TS = 6\ (M/W)(\%\ Conversion)d_\omega/100\ d_P\ D_v x(10^{-24}) \quad (1)$$

where M/W = weight ratio of monomer to water in the recipe
d_ω = density of water = 1.00 g/cm^3
d_P = density of PMMA = 1.175 g/cm^3
D_v in Å
TS in $(Å)^2/cm^3$

RESULTS AND DISCUSSION

Even though MMA has a much higher aqueous solubility than styrene, a similar trend in the particle size data was found between MMA and styrene (7), except that the PMMA latices were prepared at a lower level of solid content. This reflects the lower stabilization capability of the mixed-surfactants on the PMMA latices as compared to the styrene latices.

Effect of the Amounts of the Surfactants on the Latex Particle Size

Data for the volume average particle size of different recipes at 90% conversion are presented in Table 2. Tremendously larger particles with higher polydispersity (as high as 4.4 in D_w/D_n) were found for those recipes containing nonionic surfactant as the only emulsifier, as are shown in Table 3. For the mixed-surfactant or anionic surfactant system, the general trend showed that the particle size decreased with the increase in concentration of either the anionic or nonionic surfactant, and the particle size distributions were narrow (below 1.20).

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	0.75	0.90
0	—	1010	880	910	830	820
2.00	—	1030	—	1070	—	750
3.00	6990	970	—	730	—	660
4.00	2880	670	—	650	—	600
4.50	1810	—	—	—	—	—
5.50	1040	—	—	—	—	—

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	0.75	0.90
0	—	1.03	1.07	1.01	1.04	1.02
2.00	—	1.03	—	1.01	—	1.02
3.00	2.18	1.03	—	1.01	—	1.02
4.00	4.41	1.11	—	1.02	—	1.02
4.50	2.09	—	—	—	—	—
5.50	2.78	—	—	—	—	—

In each single-surfactant system, a proportional relationship exists between the total particle surface area per cm^3 at 90% conversion (TS) and the amount of surfactant (E) as follows:

$$TS = a\ E^b \tag{2}$$

where a is the intercept and b is the slope when values of log(TS) were plotted against log(E). The values of a were 1.2846×10^{21} and 5.542×10^{18} for SDS and BC-840, respectively; while the values of b were 0.1584 and 2.9542 for SDS and BC-840, respectively. The data and correlation are shown in Figure 1. Considerable difference in the stabilization capability was found between the two surfactants. A smaller amount of SDS was required to stabilize the same total surface area compared with BC-840, especially at low surfactant concentrations.

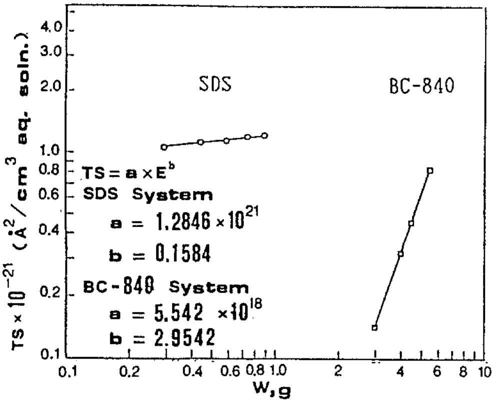

Figure 1. Correlation between the total particle surface area per cm³ aq. solution at 90% conversion. (single surfactant only)

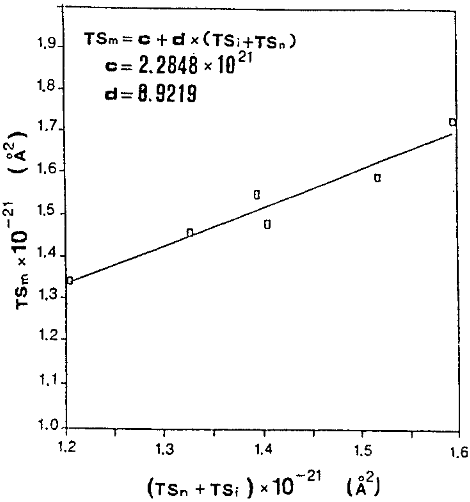

Figure 2. Total particle surface area stabilized by the mixed-surfactant per cm³ aq. solution.

A relationship close to additivity was found between TS_m and (TS_i + TS_n), where the subscripts i, n, and m denote SDS, BC-840, and the mixed-surfactant system, respectively. The values of TS_m were plotted against (TS_i + TS_n) in Figure 2. The relationship was expressed as

$$TS_m = c + d\ (TS_i + TS_n) \tag{3}$$

where c is the intercept and d is the slope. In this treatment, X grams of BC-840 has a value of TS_n, Y grams of SDS has a value of TS_i and a mixture of X grams of BC-840 and Y grams of SDS has a value of TS_m.

Combining Equations (1), (2) and (3) and replacing the constants with numerical values, we obtained equations which could be utilized to calculate the particle size of a latex produced using a mixed-surfactant recipe from the data obtained from each single surfactant recipe.

$$(D_v)_m = 1.0445 \times 10^{24} / (2.2848 \times 10^{20} + 5.1091 \times 10^{18} \times X^{2.9542} + 1.1843 \times 10^{21} \times Y^{0.1584}) \tag{4}$$

and

$$1/(D_v)_m = 2.1875 \times 10^{-4} + 0.9962 \times (1/(D_v)_n + 1/(D_v)_i) \tag{5}$$

The errors between the predicted values and the experimental values were calculated for Equations (4) and (5), as are shown in Tables 4 and 5.

The particle sizes of the latices were determined by a dynamic light scattering spectrophotometer (DLS) in this study. The accuracy of the determination may rely heavily on the software of the correlation function in the DLS. The electrical charges on the particle surface may also introduce some deviation into this determination.

Table 4
The error between the predicted values of equation (2) and the experimental values, (unit:Å).

BC-840 (g)	SDS (g)	D_v Pred., Å	D_v Expt., Å	%Error
0	0.30	984	1010	- 2.57
0	0.45	923	880	4.89
0	0.60	882	910	- 3.08
0	0.75	851	830	2.53
0	0.90	827	820	0.85
3.00	0	6426	6990	- 8.09
4.00	0	2477	2880	-13.99
4.50	0	1940	1810	7.18
5.50	0	1072	1040	3.38
				Avg. 5.17

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

BC-840 (g)	SDS (g)	$[D_v]_m$ Pred., Å	$[D_v]_m$ Expt., Å	%Error
2.00	0.30	838	1030	-18.64
2.00	0.60	768	1070	-28.22
2.00	0.90	729	750	-2.80
3.00	0.30	780	970	-19.59
3.00	0.60	719	728	-1.24
3.00	0.90	685	658	4.10
4.00	0.30	690	674	2.37
4.00	0.60	642	654	-1.83
4.00	0.90	614	602	1.99
				Avg. 8.98

Table 6
Comparison of particle size data obtained from TEM and DLS.

SDS/BC-840 and % Conversion	TEM (Å) (nm)	DLS (Å) (nm)	%Error
0.30/3.0 88.93 %	D_n = 72	D_n = 76	- 5.26
	D_v = 75	D_v = 77	- 2.60
	D_w = 82	D_w = 79	3.80
	D_w/D_n = 1.14	D_w/D_n = 1.04	
0.60/0.0 56.21 %	D_n = 67	D_n = 74	- 9.46
	D_v = 68	D_v = 75	- 9.33
	D_w = 74	D_w = 77	- 3.90
	D_w/D_n = 1.10	D_w/D_n = 1.04	
0.60/2.0 47.82 %	D_n = 75	D_n = 77	- 2.60
	D_v = 78	D_v = 78	0
	D_w = 85	D_w = 79	7.59
	D_w/D_n 1.13	D_w/D_n = 1.03	
0.60/4.0 56.42 %	D_n = 69	D_n = 74	- 6.76
	D_v = 71	D_v = 74	- 4.05
	D_w = 77	D_w = 76	1.32
	D_w/D_n 1.12	D_w/D_n = 1.03	
		Avg. %Error	D_n = 6.02
			D_v = 4.00
			D_w = 4.15

A careful examination was performed to compare the particle size data obtained from DLS with those from TEM, as are shown in Table 6. The average deviation is below 5%. This is a satisfactory result. However, this is by no means an assertion that DLS can replace all the measurements done by TEM, but rather a careful choice of DLS software and double-checking of the results with TEM should be conducted.

Variation of the Number of Particles During the Emulsion Polymerization

It has been reported (8,10) that particle number varied with conversion in the emulsion polymerization depending on whether or not sufficient emulsifier is available. Therefore, the higher concentration in emulsifier will reduce the chance of coagulation, and thus lessen the fluctuations which appear in the curves of particle number against conversion. This has been pointed out by Chu and Piirma (7) for the emulsion polymerization of styrene with a mixture of anionic and nonionic surfactants.

There are fluctuations in N in the emulsion polymerization of MMA, as are shown in Figures 3 and 4. Obviously, changes in particle number can reveal information about the stability of the latex, and the increased water-solubility of the monomer did not change the result that N varied with conversion. As was pointed out by Chu and Pirrma (7), sometimes even though no obvious coagulation is detectable by the naked eye during the polymerization, the particle number can change.

Particle Size Distribution versus Conversion

Fluctuations in the particle size distribution during the polymerization are shown in Figure 5. It is found that the index oscil-

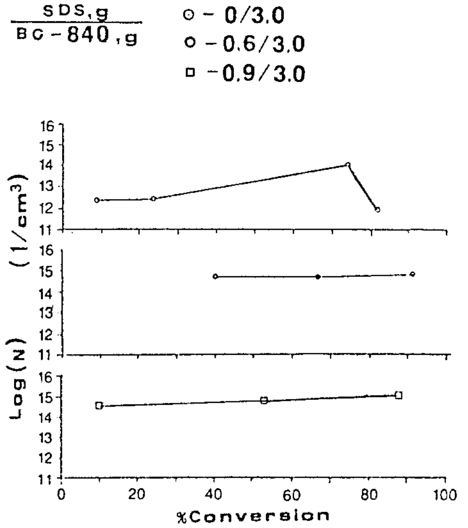

Figure 3. Effect of varying the amount of anionic surfactant with a fixed amount of nonionic surfactant, particle number per cm³ aq. solution vs. percent conversion.

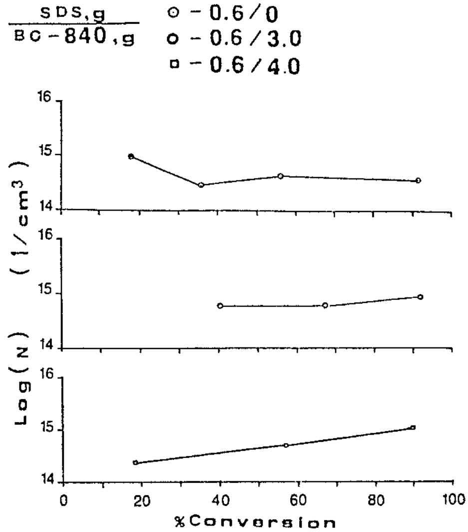

Figure 4. Effect of varying the amount of nonionic surfactant with a fixed amount of anionic surfactant, particle number per cm³ aq. solution vs. percent conversion.

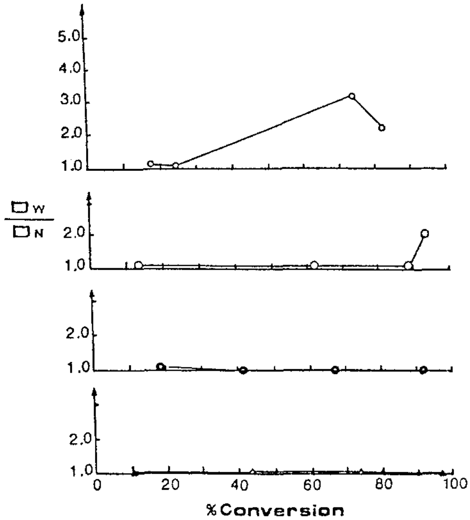

Figure 5. The variation of the polydispersity of the particle diameter during the polymerization.

lates greatly in the single surfactant system of BC-840, while the addition of SDS can reduce the oscillation.

It can be stated that there is a dynamic equilibrium among particle nucleation, particle growth and particle coagulation. The frequency of the period of the above process can affect the extent of fluctuation in the polydispersity index during the polymerization. The more frequent the occurrence of this period of particle nucleation, particle growth and particle coagulation will lead to a low polydispersity and less fluctuation. This can be seen in the polymerization using the anionic surfactant or mixed-surfactant, where the particle number increases steadily with conversion.

Emulsion Polymerization with higher (M/W)

Comparatively poorer stability was obtained in the emulsion polymerization of MMA, where lower solid contents or higher amounts of emulsifier needed to be used to avoid the formation of gel (or paste). However, as long as no paste formed, stable latices were produced. It is known that MMA has a high solubility in water and that homogeneous nucleation plays an important role in its emulsion polymerization. It has also been reported that PMMA could dissolve in its own monomer and form a more viscous emulsion (9). This "sticky stste" might have an adverse effect on the particle stability.

The following example illustrates the stabilization effect of the surfactant. Experiments with a (M/W) ratio of 25/55 were conducted in a shaker, where poor agitation was obtained, and a paste was formed during the emulsion polymerization. As is shown in Figure 6. the paste formed at higher conversions, when higher concentrations of surfactant are used.

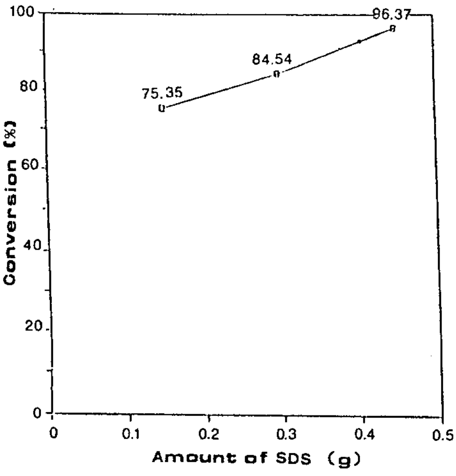

Figure 6. Paste forms at higher conversions when the higher amounts of anionic surfactant used. (MMA/H_2O = 25/55 and shaker agitation)

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