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Characteristics of emulsion polymerization of cyclohexyl methacrylate

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SUMMARY

A correlation between the particle size and the amounts of surfactants was found to fit well for the mixed-surfactant system of sodium dodecyl sulfate (SDS) and Emulphogene BC-840 (a nonionic surfactant) using in the emulsion polymerization of cyclohexyl methacrylate (CHMA) at 50°C. The formation of microglobules at early conversion was found. The effect of initiator ($K_2S_2O_8$) content and the water solubility of CHMA and PCHMA were also studied.

INTRODUCTION

The preparation of monodisperse latices by using a mixture of anionic and nonionic surfactants has been reported previously (1,2). The synergistic effect of using mixed-surfactants on latex stability has also been investigated (2-8).

Chu et al. (6-8) have performed a series of studies on the stabilization effect of mixed-surfactants in emulsion polymerization. A unifying approach has been applied on a series of monomers. As shown in Table 1, various order dependence of total particle surface area per cm^3 of aqueous phase (TS, Å^2/cm^3) on the content (E, g) of each surfactant has been determined. A correlation between the volume-average particle diameter (D_v) and the content of each surfactant has also been formulated for each system.

In this study, the emulsion polymerization of cyclohexyl methacrylate (CHMA) using different combinations of anionic surfactant (SDS) and nonionic surfactant (BC-840) was investigated. So was the water solubility of CHMA. Besides the characteristics reflected by the correlation, the emulsion polymerization of this monomer exhibits: (i) microbules formation in the beginning of polymerization; (ii) easy paste formation in the single-surfactant system of BC-840; and (iii) different order dependences of polymerization rate (R_p) and particle number (N) on initiator ($K_2S_2O_8$, KPS) content.

EXPERIMENTAL

Materials

The CHMA monomer was washed with aqueous sodium hydroxide solution followed by doubly-distilled water, dried over anhydrous sodium sulphate, vacuum-distilled, and stored at 5°C until used. Water for the polymerization process was doubly distilled. The nonionic surfactant (Emulphogene BC-840, $C_{13}H_{27}O(CH_2CH_2O)_{15}H$) was treated by

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Table 1
Comparisons of values of "a" (in $Å^2/cm^3$) and "b" in $TS = a E^b$ for different monomer systems (at 50°C)

	SDS	BC-840	Water solubility of monomer (at t°C)
styrene (6)	$a=3.37 \times 10^{21}$ $b= 0.0792$	$a=3.79 \times 10^{20}$ $b=1.00$	0.036% wt (45°C)
MMA (7)	$a=1.28 \times 10^{21}$ $b= 0.158$	$a=5.54 \times 10^{18}$ $b=2.95$	1.50% wt (45°C)
BA (8)	$a=1.26 \times 10^{21}$ $b= 0.318$	$a=4.68 \times 10^{20}$ $b=0.556$	0.32% wt (20°C)

heating at 70°C overnight under vacuum to destroy any peroxides. All others were used as received.

Polymerization

Polymerizations were conducted in 250 ml fourneck round-bottom flasks at 50°C in a constant temperature bath, as was described previously (7). 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. A typical polymerization recipe is shown in Table 2. The recipe for studying the effect of mixed-surfactants contains X grams of BC-840 and Y grams of SDS, where X ranged from 0g to 7.00g (8.14 mmol) and Y ranged from 0g to 0.75g (2.60 mmol). The critical micelle concentration (CMC) for SDS and BC-840 are 0.38g (1.32 mmol) and 0.05g (0.058 mmol) per 165g of water, respectively. The polymerization rate was determined from the slope of the conversion-time curve at the constant rate region.

Particle Size Analysis

The particle size was measured with a Photal 3000/3100 dynamic light scattering spectrophotometer (DLS), and some data were double-checked with a Jeol JEM-200CX Transmission Electron Microscope (TEM). In carrying out the DLS measurement, each determination was repeated at least twice. The random error for most of the particle size determinated by DLS for monodisperse samples is within 4% in our study. The computation of the number-average diameter (D_n), volume-average diameter (D_v), and weight-average diameter (D_w) followed the same formulas as those mentioned in Ref. 6. The number of particles per cm^3 of aqueous phase (N) and the total particle surface area per cm^3 of aqueous phase (TS) were calculated as follows:

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

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

where d_p is the density of PCHMA (1.1 $g \cdot cm^{-3}$); d_w is the density of water (1.0 $g \cdot cm^{-3}$); (M/W) is the initial weight ratio of monomer to water; and D_v in Å.

Table 2
Polymerization recipe at 50°C

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

CHMA phase was determined by polymerizing in a closed container in oven at 80°C for 5 hrs, using excess amount (e.g., 0.1g) of AIBN; and deciding the residual water content. The solubility of CHMA in the water phase was determined by the UV technique, using the absorbance at a wave length of 290 nm.

Solubility of PCHMA in Water

Ten grams of PCHMA was mixed with 100g of water using end-over-end agitation at 50°C for 1 hr. Then the mixture was filtered. The filtrate was dried to determine the solid content, and, therefore, the dissolved PCHMA.

Solubility of PCHMA in CHMA

Fifty grams of CHMA with 60 ppm of hydroquinone was mixed end-over-end with different amounts of PCHMA (i.e. 10, 20, 30, 40 and 50g) at 50°C, for 1 hr to see if the PCHMA was dissolved.

RESULTS AND DISCUSSION

Stabilizing effect of surfactants

Data of the volume average particle size (D_v) determined at around 90% conversion are shown in Table 3. Data of particle size distribution (D_w/D_n) of corresponding latices are all below 1.1. In both single-surfactant systems, particle size decreases with increasing amount of surfactant. Note that all the particle size data for the nonionic surfactant system are below 900 Å at each surfactant level. These particle sizes are far smaller than those of other monomers, such as MMA, using the same surfactants and recipes, as reported by Wang and Chu (7). It is generally accepted that the increase of surfactant concentration will produce a smaller particle size latex, as more stabilizer will be present to cover the increasing surface area (9).

The total particle surface area per cm^3 of aqueous phase (TS), which is a reciprocal function of particle diameter as shown in Eq. 2, was utilized to represent the stabilization efficiency of a surfactant. In other words, the emulsifiers are considered to have a higher stabilizing efficiency if the latex particles formed have a larger TS value.

In each single-surfactant system, a relationship between the TS value and the amount (g) of surfactant (E) is correlated as follows:

$$TS = a\,E^b \qquad (3)$$

where "a" is the intercept and "b" is the slope when values of log(TS) are plotted against log(E). In this study, the values of "a" were found to be 1.37×10^{21} and 8.19×10^{20} ($Å^2/cm^3$) for SDS and BC-840, respectively; while the values of "b" were 0.244 and 0.424 for SDS

Table 3
Volume-average particle diameter at about 90% conversion, (in Å)

Nonionic Surfactant, BC-840 (g)	Anionic Surfactant, SDS (g)				
	0	0.30	0.45	0.60	0.75
0	—	1130	950	930	870
1.00	—	730	800	710	—
2.00	—	810	730	710	—
3.00	860	710	740	720	—
3.50	830	810	650	700	—
3.75	760	—	—	—	—
4.50	730	—	—	—	—
5.00	700	—	—	—	—
7.00	600	—	—	—	—

and BC-840, respectively. This reveals that to stabilize the same total particle surfacearea, much more BC-840 is required than SDS.

Table 1 shows the comparisons of values of "a" and "b" in Eq. 3 for different monomer systems. The exponent "b" for both SDS and BC-840 on CHMA are comparatively close to those on n-butyl acrylate (BA). Note that the solubility of CHMA in water is smaller than that of BA, as will be shown later.

For the mixed-surfactant system, a relationship was used to correlate 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 relationship was considered as follows:

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

Substituting Eqs. 3 and 2 into Eq. 4, we obtained Eqs. 5 and 6, as follows:

$$[D_v]_m = 1.12\text{x}10^{24}/[2.40\text{x}10^{20} + 4.43\text{x}10^{20}\ X^{0.424} + 7.41\text{x}10^{20}\ Y^{0.244}] \qquad (5)$$

and

$$1/[D_v]_m = 2.14\text{x}10^{-4} + 0.541\ (1/[D_v]_n + 1/[D_v]_i) \qquad (6)$$

Here, X and Y represent the amounts (g) of BC-840 and SDS, respectively, in the recipes.

The deviations between the correlated values and the experimental values for Eqs. 5 and 6, are 7.9%. and 9.2%, respectively, as shown in Tables 4 and 5.

Paste formation

In some recipes, the latex became a paste at high conversions. The paste is able to redisperse by dilution. The same kind of paste has been found in the emulsion polymerization of other monomers, such as MMA (7). The paste formed at higher conversios in the polymerization when the higher amounts of nonionic surfactant (BC-840) were used, as shown in Fig. 1; but no paste formed when the content of BC-840 was larger than 3.75g. In comparison, recipes using SDS did not form paste in the reaction.

Table 4
Error between the predicted values of Eq. 5 and the experimental values

X(g)	Y(g)	$[D_v]_m$ Pred. Å	$[D_v]_m$ Expt. Å	% Error
1.00	0.30	970	730	24.2
1.00	0.45	866	800	8.3
1.00	0.60	838	710	18.0
2.00	0.30	808	810	-0.2
2.00	0.45	776	730	6.3
2.00	0.60	752	710	5.9
3.00	0.30	748	710	5.4
3.00	0.45	720	740	-2.7
3.00	0.60	700	720	-2.8
3.50	0.30	725	810	-10.5
3.50	0.45	699	650	7.5
3.50	0.60	680	700	-2.9
			Avg.	7.9

Table 5
Error between the predicted values of Eq. 6 and the experimental values

X(g)	Y(g)	$[D_v]_m$ Pred. Å	$[D_v]_m$ Expt. Å	% Error
3.00	0.30	757	710	6.6
3.00	0.45	708	740	-4.3
3.00	0.60	702	720	-2.5
3.50	0.30	652	810	-19.5
3.50	0.45	589	650	-9.4
3.50	0.60	610	700	-12.9
			Avg.	9.2

The mechanism of paste formation in emulsion polymerization is attributed to the agglomeration of particles (10). The paste was often formed at recipes with higher solid content and a rapid increase in viscosity was detected before the formation of paste (10). For the system of MMA, in the presence of SDS, the gel forms when the reduced thickness (δ/r, i.e., thickness/radius of particles) of hydrodynamic layer exceeds 3.0 (10). The agglomeration process may be a synonym to the reversible flocculation (11), which has been found long time ago in the creaming process of a natural rubber latex by adding sodium alginate (12). The type of flocculation was reversed by dilution and the latex could be taken through the aggregation-redispersion-aggregation cycle many times.

Effect of initiator content

The electrostatic effect of the initiator on the stability of polymer latices has been investigated before (13-15). It was shown that the sulphate end group of a polymer chain stays on the particle surface and has a stabilizing effect on the latex particles.

Results of this study showed that the particle size decreases with increasing content of KPS, regardless either SDS or BC-840 was used and the polymerization rate increases with [I], as shown in Table 6.

Rough estimation of the order dependences of both R_p and N on [I] for SDS and BC-840 systems are shown as that: $R_p \sim [I]^{0.64}$ and

Table 6

Effect of amount of initiator ($K_2S_2O_8$) on the D_v(Å) of the latices at about 90% conversion and the polymerization rate (R_p, x10^5 mol/ml·min)

		$K_2S_2O_8$ (g) 0.0376	0.188	0.94
SDS (0.60g)				
	D_v	950	930	740
	R_p	0.855	3.76	6.70
BC-840 (5.00g)				
	D_v	760	700	650
	R_p	0.766	5.08	9.34

$N \sim [I]^{0.23}$ for recipes with 0.60g of SDS; and $R_p \sim [I]^{0.78}$ and $N \sim [I]^{0.16}$ for recipes with 5.00g of BC-840.

The order dependences of R_p on [I] are greater than 0.4, while those of N on [I] are smaller than 0.4. This may reflect that the greater number of radicals, generated by the greater [I], was entering particles, but the the particle number is increase limitedly. This leads to the average number of radicals per particle, $\bar{n}$, to be greater than 0.5 in these recipes.

Although the water solubility of monomer is higher and surfactant contents are lower in the emulsion polymerization of n-butyl acrylate (BA) (16), the great discrepancy in order dependence has been found. The order dependences of R_p and N on [I] are shown as that:
$R_p \sim [I]^{0.62}$ and $N \sim [I]^{0.40}$ for recipes with 0.45g of SDS; and
$R_p \sim [I]^{0.69}$ and $N \sim [I]^{0.21}$ for recipes with 2.0g of BC-840.

Microbule formation at early conversions

The formation of microglobules was observed in the runs where recipes containing the lowest initiator content (i.e. 0.0376g). The particles were small at early conversions (i.e. 140 Å) compared to those at higher conversions (i.e. 640- 680 Å), as shown in Fig. 2. It

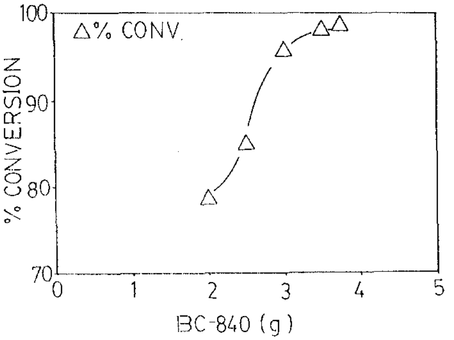

Fig. 1. Paste formed at higher conversions when the higher amounts of BC-840 were used

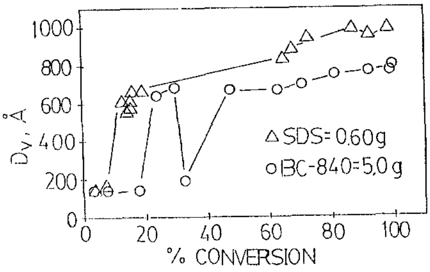

Fig. 2. Variations of particle diameter (D_v, Å) in the polymerization for recipes containing 0.0376g of KPS

Table 7
Solubility Data

CHMA in water	0.016% wt
water in CHMA	1.2% wt
PCHMA in water	0.022% wt
PCHMA in CHMA	> 50% wt

was found that the particle size increased fourfold in a short period of time. Similar case has been found in the recipe containing 0.30g of SDS (single-surfactant). This indicates the aggregation of primary particles at the early stage of the emulsion polymerization. The aggregation process has been found by Hergeth et al. (17-19) for emulsion polymerization of vinyl acetate, MMA and styrene. This has also been reported as the flocculation of microglobules (20, 21). A second nucleation makes the average particle diameter drop at 33% conversion for the case of BC-840, as shown in Fig. 2. This has been observed quite often for the emulsion polymerization using BC-840 as the emulsifier (22).

The butyl methacrylate (BMA) (20) (which is slightly soluble in water with solubility of 0.078% vol. at 25°C) does not seem to form microglobules. Note that the CHMA has a structure that closer to BMA, but does form microglobules.

It is believed that the micellar nucleation mechanism dominates the microglobule formation process. Since both the CHMA and PCHMA have low solubility in water, as shown in Table 7; the chance for the homogeneous nucleation is comparatively low. Furthermore, for most of the recipes, surfactant concentrations are above CMC, and therefore, the micellar nucleation mechanism is expected to predominate. It has been pointed out (23) that the micellar nucleation mechanism predominates in the emulsion polymerization once the surfactant concentration is above CMC, despiting that a monomer of high water-solubility may be nucleated homogeneously. However, the homogeneous nucleation mechanism can not be excluded since the emulsion polymerization can be conducted with surfactant concentration below CMC (e.g., the recipe containing 0.30g of SDS in the single-surfactant system).

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