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POLYMERIZATION OF METHYL METHACRYLATE AND ISOBUTYL METHACRYLATE IN TERNARY-COMPONENT EMULSIONS AND MICROEMULSIONS: EFFECT OF SURFACTANT CONCENTRATION

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Key Words: Methyl methacrylate; Isobutyl methacrylate; Ternary-component emulsions and microemulsions

ABSTRACT

The similarities and differences in the polymerization of MMA (methyl methacrylate) and iBMA (isobutyl methacrylate) in a ternary-component system have been investigated from a turbid emulsion to a transparent microemulsion by increasing the surfactant concentration. In spite of the difference in the solubilities of these two monomers in the aqueous phase, the rate dependencies on the surfactant concentration of both monomers were found to be about 0.30 for the emulsion polymerization and about 0.60 for the microemulsion polymerization with monomer concentrations higher than 5 wt%. However, at a low monomer concentration (3 wt%), different negative rate dependencies of −0.93 and −1.20 were obtained for microemulsion polymerization of MMA and iBMA, respectively. The results are discussed in terms of particle nucleation mechanisms.

INTRODUCTION

Emulsion polymerization has been extensively studied for many decades, but the first microemulsion polymerization study was only reported in 1980 by Stoffer and Bone [1]. Since then, the microemulsion polymerization of methyl methacrylate (MMA) or of styrene has been increasingly investigated in oil-in-water microemulsions [2–11] which required a cosurfactant in conjunction with a surfactant. Only recently, ternary-component microemulsion systems [12–16] which do not need a cosurfactant have been successfully used for the polymerization of styrene and of MMA.

With the use of a suitable ternary-component system, it is possible to investigate the polymerization of some monomers in both emulsions and microemulsions using three identical components, i.e., monomer, water, and surfactant. Such a ternary system can be continuously changed from turbid emulsions to transparent microemulsions by simply increasing the surfactant concentration. We recently reported [17] the polymerization of MMA in such a ternary system covering both emulsions and microemulsions. The ternary system consisted of MMA, water, and a cationic surfactant of cetyltrimethylammonium bromide (CTAB). Stable PMMA latexes (16–30 nm in hydrodynamic radius) were obtained from both emulsion and microemulsion polymerizations initiated by potassium persulfate (KPS). The low dependency of polymerization rate (R_p) on $[\mathrm{CTAB}]^{0.31}$ and its strong dependency on $[\mathrm{KPS}]^{0.82}$ were observed for the emulsion polymerization of MMA in contrast with those of $[\mathrm{CTAB}]^{0.58}$ and $[\mathrm{KPS}]^{0.33}$ for microemulsion polymerization.

A more extensive study of MMA polymerization, including the effect of MMA concentration on R_p, in the ternary emulsions and microemulsions is presented in this paper in conjunction with a comparative study on the less water-soluble isobutyl methacrylate (iBMA).

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (Fluka) and isobutyl methacrylate (iBMA) (TCI) were vacuum-distilled before use. Cetyltrimethylammonium bromide (CTAB) from Fluka was recrystallized from a distilled ethanol–acetone mixture (1:3 by volume). Potassium persulfate (Fluka) was recrystallized from distilled water.

Phase Diagram of Three-Component System

The clear region (o/w microemulsion) was determined visually by titration of the monomer and CTAB mixture in a screw-capped tube at 30°C. It was thoroughly mixed with a vortex mixer. The clear–turbid boundaries were established from systematic titrations.

Polymerization

The polymerization of both MMA and iBMA with the compositions from both clear and turbid regions was carried out in a glass dilatometer immersed in a 60 ± 0.1°C water bath. The emulsion/microemulsion contained in a ground-glass tube was first degassed at 10 torr for one freeze–thaw cycle. It was then transferred directly into a dilatometer which was attached to a vacuum line. The change of the liquid level in the capillary of the dilatometer was monitored by a cathetometer as a function of time. The fractional conversion of the monomer was determined from the volume change which was calculated from the height of the capillary.

After polymerization, the polymer was precipitated in a large quantity of distilled methanol. It was then washed repeatedly with distilled methanol and water in order to remove the residual CTAB. The conductivity of the washing was measured periodically in order to determine the cleanliness of the polymer obtained.

Molecular Weight Determination

Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Waters 410 liquid chromatography system equipped with a Waters 410 differential refractometer. The columns used were Varian micropak TSK 7000H and GMH6 in series, and the eluent was degassed tetrahydrofuran (THF) which contained 0.025% 2,6-di-*tert*-butyl-*p*-cresol as a stabilizer. The flow rate was maintained at 0.8 mL/min. Polystyrene standards (Polyscience) (0.2 mg/mL in THF) were used for calibration.

Particle Size Determination

Particle sizes of the polymerized microemulsion and emulsion latexes were measured by quasi-elastic light scattering (QLS) using a Malvern 4700 light-scattering spectrophotometer. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate. Prior to measurements, the latexes were diluted with distilled water until the volume fractions of particles were in the 0.01 to 0.1 range. The hydrodynamic radius of latex particles (R_h) was calculated from the intrinsic diffusion coefficient (D_0) using the well-known Stokes-Einstein equation.

RESULTS

Partial Phase Diagrams of Ternary o/w Microemulsions

Figure 1 shows the partial phase diagrams of two ternary systems, MMA/CTAB/H_2O and iBMA/CTAB/H_2O. The shaded area "E" represents the turbid emulsion region. The enclosed clear regions labeled "M" are transparent microemulsions. At higher CTAB concentrations, the shaded area "L" is the viscous crystalline region. A certain composition line can be drawn from a fixed weight ratio of water/monomer to the apex of CTAB such as "Line A" in Fig. 1. Similarly, other suitable composition lines can also be drawn from other fixed weight ratios of water/monomer. By doing so, the effect of the surfactant concentration on the polymerization

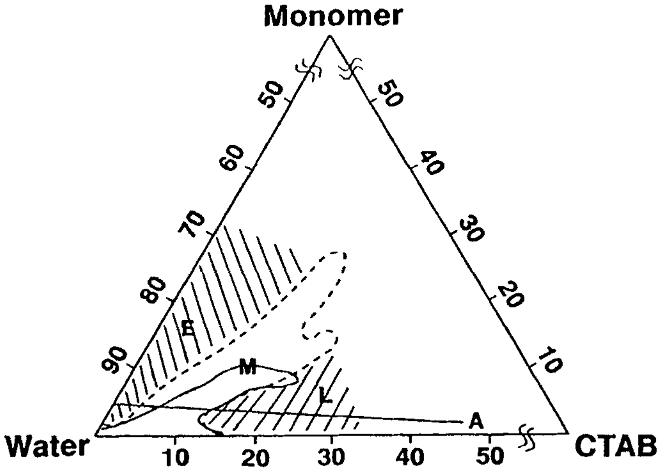

FIG. 1. Partial phase diagrams (at 30°C) of ternary systems consisting of water/CTAB/different monomers: (---) MMA; (—) iBMA.

of a monomer from emulsions (E) to microemulsions (M) at different water/monomer weight ratios can be studied. Compositions from the transparent region spontaneously form microemulsions upon mixing. It is noted that the microemulsion region for the MMA system is larger than that of iBMA. This may be related to the polarity of the monomer and its solubility in water. The solubilities of MMA [18] and iBMA [19] in water are 1.5, and 0.023 (v/v %), respectively. The relatively polar MMA molecules may also function as cosurfactant molecules [16] which interdisperse in the palisade layers of surfactant/water interfaces. The electrostatic repulsion between positively charged head groups of CTAB molecules is thus reduced, which favors the formation of small microemulsion droplets of MMA. Since iBMA is relatively less polar than MMA, it may reside closer to the hydrophobic cores of the microemulsion droplets.

Polymerization of MMA

As shown in Table 1, the compositions used for the polymerization study were based on four weight ratios of water/MMA of 32.4, 18.8, and 13.3, and 9.0, designated as Series A, B, C, and D, respectively. This means that the MMA concentration increased from about 3 to 10 wt% as the CTAB concentration for each series increased from 1 to about 12 wt%, and the system changed progressively from turbid emulsions to transparent microemulsions. The boundary between emulsion and microemulsion for each series shifted to a higher surfactant concentration when the MMA concentration was increased from Series A to D. For example, only about 4 wt% CTAB was needed to form a transparent microemulsion containing about 3 wt% MMA for Series A, while the formation of a microemulsion containing approximate 9 wt% MMA (Series D) required about 8 wt% CTAB. However, all samples including turbid emulsions (Table 1) became translucent and stable after polymerization.

TABLE 1. Compositions for MMA Polymerization in Ternary Systems[a]

System	CTAB, wt%	MMA, wt%	Water, wt%	Water/ MMA	Appearance of the system at 30°C before polymerization
A1	1.00	2.96	96.04	32.4	T
A2	2.00	2.93	95.07	32.4	T
A3	3.00	2.90	94.10	32.4	T
A4	4.00	2.87	93.13	32.4	C
A5	5.00	2.84	92.16	32.4	C
A6	6.00	2.81	91.19	32.4	C
A7	8.00	2.75	89.25	32.4	C
A8	9.18	2.72	88.10	32.4	C
A9	10.00	2.69	87.31	32.4	C
B1	1.00	5.00	94.00	18.8	T
B2	2.00	4.95	93.05	18.8	T
B3	3.00	4.90	92.10	18.8	T
B4	5.00	4.80	90.20	18.8	C
B5	7.00	4.70	88.30	18.8	C
B6	8.00	4.65	87.35	18.8	C
B7	9.00	4.60	86.40	18.8	C
B8	11.00	4.50	84.50	18.8	C
C1	1.00	6.93	92.70	13.3	T
C2	2.00	6.86	91.14	13.3	T
C3	3.00	6.79	90.21	13.3	T
C4	6.00	6.58	87.42	13.3	C
C5	8.00	6.44	85.56	13.3	C
C6	8.77	6.38	84.85	13.3	C
C7	10.00	6.30	83.70	13.3	C
C8	11.00	6.23	82.77	13.3	C
D1	3.00	9.70	87.30	9.0	T
D2	4.00	9.60	86.40	9.0	T
D3	5.00	9.50	85.50	9.0	T
D4	7.00	9.30	83.70	9.0	T
D5	10.00	9.00	81.00	9.0	C
D6	11.00	8.90	80.10	9.0	C
D7	12.00	8.80	79.20	9.0	C

[a] T = turbid (emulsion); C = clear fluid (microemulsion). All four series were polymerized at 60°C using 0.6 mM KPS (based on water). After polymerization, all samples become translucent and stable latexes.

As illustrated in Fig. 2, the polymerization rate–conversion curves show three distinct regions (Intervals I, II, and III) for the emulsion polymerization of MMA at relatively low CTAB concentrations (Samples B1 and D1). But the rate plateau region (Interval II) disappeared in microemulsion polymerization of MMA at relatively high CTAB concentrations (Samples B6, C5, and D5). This is consistent with the general observations for other emulsion and microemulsion polymerizations studied previously.

The effect of CTAB concentration on the initial rate of polymerization at about 5% conversion $(R_p)_i$ for Series A, C, and D is shown in Fig. 3. In order to normalize the small variation of MMA concentration used in each series, Fig. 3 is plotted as log $(R_p)_i$ against log([CTAB]/[MMA]) instead of log[CTAB]. In general, log$(R_p)_i$ for each series increased linearly with the increase of log([CTAB]/[MMA]) in the emulsion region up to the boundary region between emulsion and microemulsion. Log$(R_p)_i$ then decreased significantly in the microemulsion region, especially for the system (Series A) containing a low MMA concentration (3 wt% MMA). However, it is interesting to note that $(R_p)_i$ increased slightly again in the microemulsion regions for the systems (Series B, C, and D) with higher MMA concentrations (>5 wt% MMA). Although the values of $(R_p)_i$ were higher for those series with higher MMA contents as expected, the gradients of the linear log plots were about the same for the emulsion polymerizations. It is thus established that $(R_p)_i$ generally varied with $[\text{CTAB}]^{0.26-0.31}$ for the emulsion polymerization of MMA. But a strong negative dependency of $(R_p)_i$ on $[\text{CTAB}]^{-0.93}$ was obtained for the microemulsion polymerization of low MMA concentration (3 wt%) such as Series A. At higher MMA concentrations (5 < MMA < 10 wt%), $(R_p)_i$ in the microemulsion region first showed a negative and then a positive dependency on the

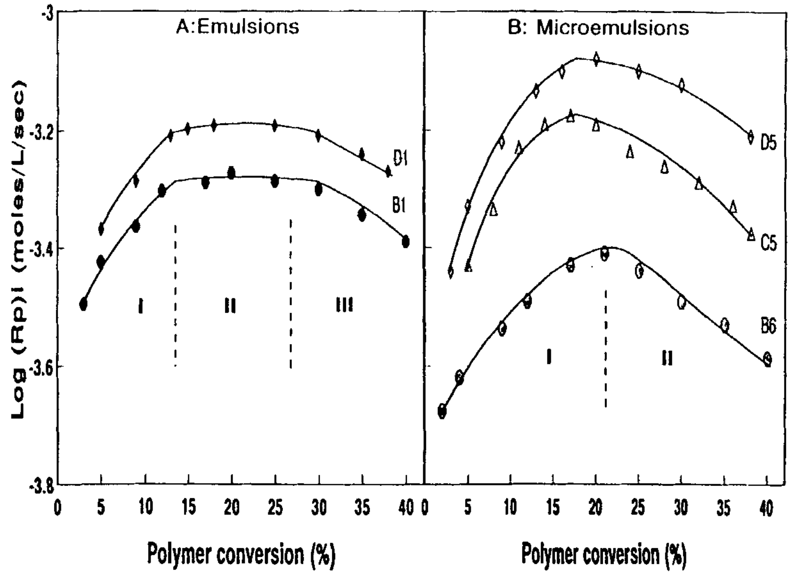

FIG. 2. MMA polymerization rate curves at 60°C for emulsions (Samples B1 and D1) and microemulsions (Samples B6, C5, and D5) at different MMA concentrations.

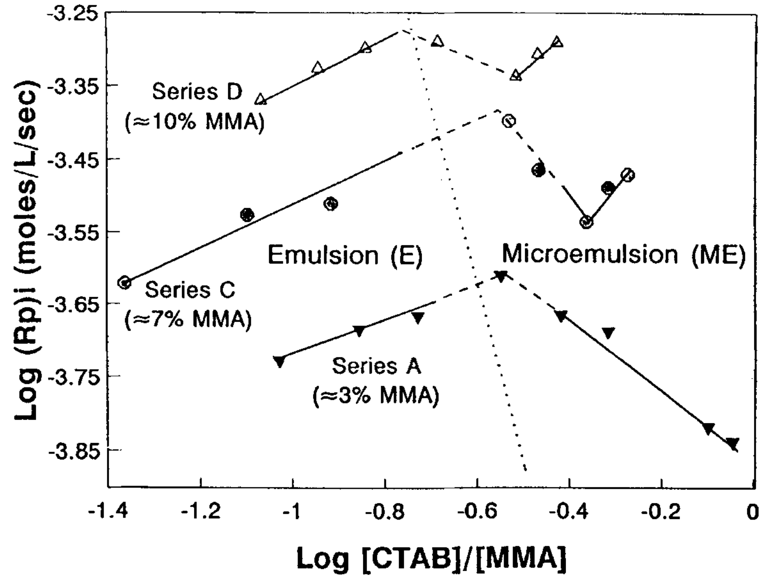

FIG. 3. Effect of CTAB concentration on the initial rate of polymerization of MMA at different monomer concentrations. The dotted line is a rough indication of the boundary between the emulsion and the microemulsion regions.

CTAB concentration. The region for negative dependency became less obvious when the MMA concentration approached 10 wt%. The positive dependency of $[\mathrm{CTAB}]^{0.58-0.60}$ for the microemulsion polymerization of MMA was only obtained for the systems (Series B, C, and D) which contained 5 to 10 wt% MMA.

The effect of CTAB concentration on R_h and other properties of PMMA latexes is summarized in Table 2. Those not measured are indicated by a dash. R_h of latexes for Series A to D decreased quite similarly as the CTAB concentration was increased from 1 to about 6 wt% in the emulsion regions. All R_h were at their minima in the CTAB concentration range of about 8-9 wt%, but they increased again with a further increase of CTAB concentration in the microemulsion region, an effect particularly pronounced for Series D.

The number of polymer particles per milliliter of the final latex (N_d) was calculated from the volume fraction of the latex. Figure 4 shows the effect of CTAB concentration on N_d. N_d varied with the ~1.20 power of CTAB concentration up to about 9 wt% CTAB, and then it decreased in the higher (>9 wt%) CTAB concentration region. For a very low MMA concentration, ca. 3 wt% of Series A, M_w decreased from the emulsion to the microemulsion regions as seen in Table 2. To avoid confusion, only M_ws of Series A in the microemulsion region are plotted in Fig. 5. The effect of CTAB concentration on M_w obtained from both emulsion and microemulsion polymerization was only marginal for Series B (ca. 5 wt% MMA), i.e., $M_w \propto [\mathrm{CTAB}]^{0.03}$, as can be in Fig. 5, but it was almost unaffected by the surfactant concentration for the system with higher MMA concentrations, such as for Series C (ca. 7 wt% MMA).

TABLE 2. Effect of CTAB Concentration on Some Properties of PMMA Latexes

System	CTAB, wt%	R_h, nm	N_d, 10^{15} mL^{-1}	M_w, 10^6	M_w/M_n
A1	1.00	20.0	1.00	6.4	4.4
A2	2.00	18.5	1.60	6.3	4.6
A3	3.00	17.1	2.50	–	–
A4	4.00	19.7	1.90	–	–
A5	5.00	14.6	5.20	5.3	5.3
A6	6.00	12.9	8.50	4.9	6.7
A7	8.00	12.6	11.00	4.2	7.1
A8	9.18	12.6	13.00	–	–
A9	10.00	14.8	8.20	–	–
B1	1.00	25.4	0.89	–	–
B2	2.00	24.1	1.08	–	–
B3	3.00	22.9	1.41	5.0	4.9
B4	5.00	19.6	2.76	5.8	4.0
B5	7.00	17.0	5.10	6.1	3.6
B7	9.00	15.8	7.39	6.2	3.6
B8	11.00	24.8	2.21	–	–
C1	1.00	36.0	0.33	6.7	4.6
C2	2.00	26.6	1.00	7.1	4.3
C3	3.00	27.9	0.95	–	–
C5	8.00	25.0	1.90	–	–
C6	8.77	23.0	2.60	7.3	5.2
C7	10.00	23.5	2.60	7.4	5.6
D1	3.00	31.8	0.91	–	–
D2	4.00	30.5	1.01	–	–
D3	5.00	26.7	1.62	–	–
D5	10.00	25.4	2.36	–	–
D6	11.00	30.4	1.48	–	–
D7	12.00	38.2	0.84	–	–

Polymerization of iBMA

In conjunction with the polymerization of MMA, a much less polar monomer isobutyl methacrylate (iBMA) was chosen for comparison. The propagation rate coefficient for iBMA is comparable to that of MMA, but its water solubility (0.023 v/v %) is much smaller than that of MMA (1.5 v/v %).

Table 3 lists the two series of compositions, covering both emulsions and microemulsions, which have been studied. Since the microemulsion region for

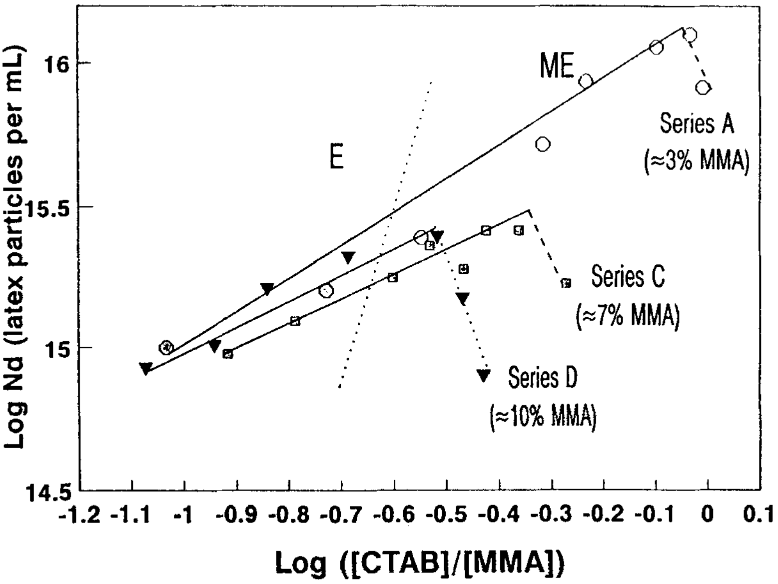

FIG. 4. Effect of CTAB concentration on number of PMMA particles per mL latex (N_d) at different monomer concentrations.

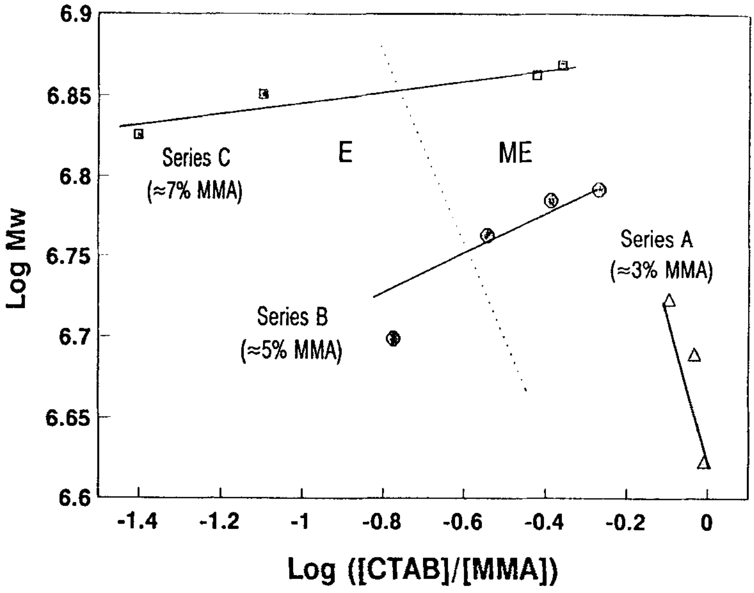

FIG. 5. Effect of CTAB concentration on molecular weights of PMMA at different monomer concentrations.

TABLE 3. Compositions for Polymerization of iBMA in Ternary Systems[a]

System	CTAB, wt%	iBMA, wt%	Water, wt%	Water/ iBMA	Appearance of the system at 30°C before polymerization
E1	1.00	2.97	96.03	32.3	T
E2	2.00	2.94	95.06	32.3	T
E3	3.00	2.91	94.09	32.3	T
E4	4.00	2.88	93.12	32.3	T
E5	6.00	2.82	91.18	32.3	C
E6	8.00	2.76	89.24	32.3	C
E7	9.00	2.73	88.27	32.3	C
E8	10.00	2.70	87.30	32.3	C
F1	2.00	4.90	93.10	19.0	T
F2	4.00	4.80	91.20	19.0	T
F3	6.00	4.70	89.30	19.0	T
F4	8.00	4.60	87.40	19.0	C
F5	10.00	4.50	85.50	19.0	C
F6	11.00	4.45	84.55	19.0	C
F7	12.00	4.40	83.60	19.0	C
F8	13.00	4.35	82.65	19.0	C

[a]T = turbid (emulsion); C = clear fluid (microemulsion). Both series were polymerized at 60°C using 0.6 mM KPS (based on water). After polymerization, all samples become translucent and stable latexes, except Samples E1 and F1.

iBMA was much smaller than that of MMA, only four different wt% iBMAs for Series E and five for Series F were formulated with a CTAB concentration of less than 13 wt%. After polymerization, some emulsion latexes with a lower surfactant concentration (Samples E1 and F1) were very unstable. However, the other polymerized emulsions and microemulsions became translucent but were stable. Some physical properties of latex particles of PiBMA are summarized in Table 4. Those not measured are indicated by a dash.

As for the MMA polymerization, $(R_p)_i$ for iBMA polymerization in emulsions for both Series E and F increased with the CTAB concentrations as shown in Fig. 6. The logarithm relationship between $(R_p)_i$ and CTAB concentration is about 0.30. In contrast to the emulsion polymerization, an increase in the surfactant concentration for Series E and F in the microemulsion region showed an inverse effect on $(R_p)_i$ such as that observed for the MMA system. But for the system with a higher monomer concentration (~ 5 wt% for Series F), $(R_p)_i$ increased again with the relationship of $R_p \propto [\mathrm{CTAB}]^{0.60}$.

R_h for emulsion latexes decreased drastically from about 79 to 23 nm as the CTAB concentration was increased from 1 to about 6 wt%. It then decreased slowly in the microemulsion regions (6 < CTAB < 13 wt%). This is in sharp contrast

TABLE 4. Effect of CTAB Concentration on Some Properties of PiBMA Latexes

System	CTAB, wt%	R_h, nm	N_d, 10^{15} mL^{-1}	M_w, 10^6	M_w/M_n
E1	1.0	78.9	0.02	5.1	19.3
E2	2.0	66.2	0.04	4.7	15.0
E3	3.0	57.1	0.07	3.4	13.4
E4	4.0	28.8	0.63	2.7	9.2
E5	6.0	23.1	1.50	—	—
E6	8.0	19.6	3.10	—	—
E7	9.0	14.0	9.10	2.1	7.3
F1	2.0	63.6	0.06	5.1	14.9
F2	4.0	38.8	0.33	6.2	11.7
F3	6.0	28.5	1.00	5.5	12.9
F4	8.0	21.7	2.70	5.0	12.4
F5	10.0	20.4	3.70	6.0	10.5
F6	11.0	19.1	4.70	4.5	12.1
F7	12.0	18.0	6.10	5.1	11.7
F8	13.0	16.2	8.70	5.5	11.0

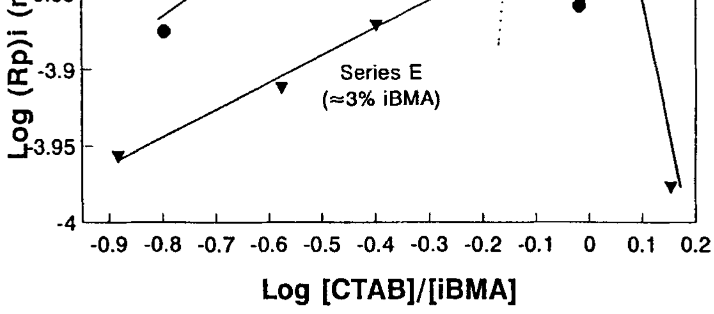

FIG. 6. Effect of CTAB on the initial rate of polymerization of iBMA at two different monomer concentrations. The dotted line is a rough indication of the boundary between the emulsion and the microemulsion regions.

with what was observed for the MMA system where R_h increased again in microemulsions with a higher CTAB concentration. The dependency of $N_d \propto [\mathrm{CTAB}]^{2.4}$ was obtained for emulsion and microemulsion polymerizations for Series E and F as shown in Fig. 7. The pronounced difference between the iBMA and MMA microemulsion polymerizations is that the former showed a strong positive dependency of N_d on the CTAB concentration while the latter exhibited a negative dependency (Fig. 4, Series D).

The effect of CTAB concentration on M_w is represented in Fig. 8. A negative relationship between log M_w and log[CTAB] was found for Series E (~3 wt% iBMA) throughout the emulsion and microemulsion regions, i.e., $M_w \propto [\mathrm{CTAB}]^{-0.45}$. Again, this negative dependency is similar to that of the MMA system for Series A (Fig. 5 and Table 2). However, there was no significant effect of CTAB concentration on M_w at a higher concentration (ca. 5%) of iBMA (Series F), similar to that observed for a higher MMA concentration system (Fig. 5, Series B and C).

DISCUSSION

The following discussion focuses on the similarities and the differences in polymerization between MMA and iBMA in a given ternary-component system. The system was varied from a turbid emulsion to a transparent microemulsion by simply changing the CTAB concentration. The effect of the monomer concentration of a relatively polar MMA and a less polar iBMA on the kinetics of polymerization is examined. The important results are summarized in Table 5 for easy comparison and discussion.

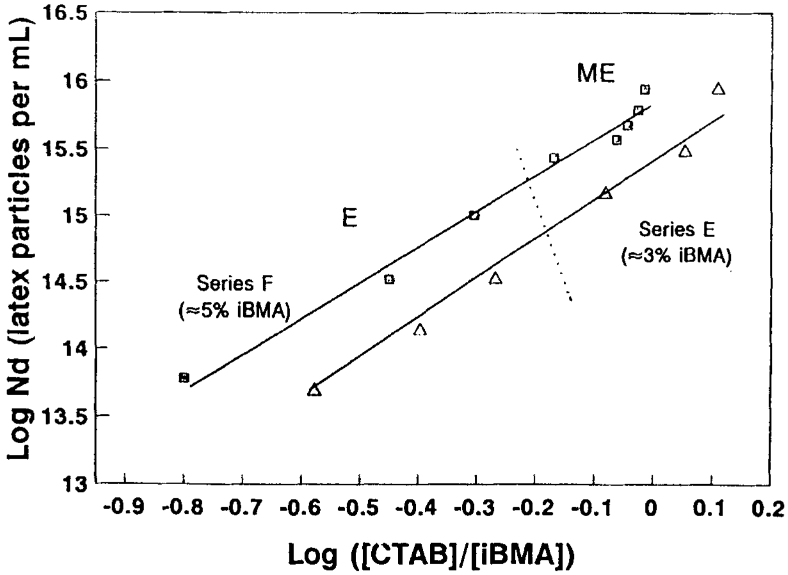

FIG. 7. Effect of CTAB concentration on number of PiBMA particles per mL latex (N_d) at different monomer concentrations.

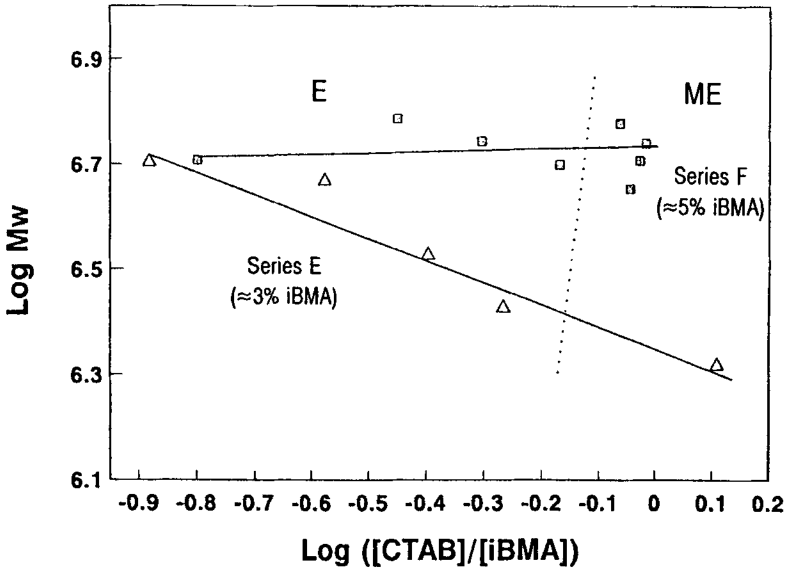

FIG. 8. Effect of CTAB concentration on molecular weights (M_w) of PiBMA at different monomer concentrations.

TABLE 5. The Effect of CTAB Concentration on Some Parameters Derived from Emulsion/Microemulsion Polymerizations of MMA and iBMA

	MMA, 3-10 wt%		iBMA, 3-5 wt%	
Parameters*	E	ME	E	ME
$(R_p)_i \propto [\text{CTAB}]^a$	0.26-0.31	0.58-0.60 (>5% MMA) −0.93 (3% MMA)	0.30	0.60 (5% iBMA) −1.20 (3% iBMA)
$N_d \propto [\text{CTAB}]^b$	1.20	−4.20 (10% MMA)	2.40	2.40
$M_w \propto [\text{CTAB}]^c$	← 0.03 → (5% MMA) ← 0 → (10% MMA)		← −0.45 → (3% iBMA) ← 0 → (5% iBMA)	

*The numbers in the columns correspond to the respective exponents of a, b, and c. Those only valid for particular monomer concentrations are specified in the parentheses. The symbols ← → indicate that the relationship is valid for both emulsion (E) and microemulsion (ME) polymerizations.

The general rate dependency for the microemulsion polymerization of both MMA and iBMA, with the monomer concentration not less than 5 wt%, is $(R_p)_i \propto [\mathrm{CTAB}]^{0.60}$. But negative rate dependency appears in the region between emulsion and microemulsion as shown in Figs. 3 and 6. When the monomer concentration is down to about 3 wt%, the negative dependencies of -0.93 and -1.20 were unambiguously obtained for MMA and iBMA, respectively. As for the emulsion polymerization of both monomers, a rather good single rate dependency of $(R_p)_i \propto [\mathrm{CTAB}]^{-0.30}$ was found for all the monomer concentrations investigated. This low rate dependency (0.30) is even smaller than that (0.47) of emulsion polymerization of butyl methacrylate [20-22] using an anionic surfactant. These results seem to indicate that the initiation mechanism in emulsion polymerization is quite different from that of microemulsion polymerization for both MMA and iBMA.

The nucleation mechanism in MMA emulsion polymerization is discussed first. In view of the relatively high MMA solubility in comparison to that of iBMA, in the aqueous phase (1.5 v/v %) free radicals generated by the water-soluble KPS were highly likely to react first with those of water-solubilized MMA to form soluble oligomeric radicals. These oligomeric radicals continued to grow by further addition of MMA units. It is estimated [23] that oligomeric radicals with 4 MMA units correspond to species with sufficient surface activity for the usual micellar entry (micellar nucleation). Alternatively, these radicals can also grow to more than 10 MMA units [23] and precipitate in the aqueous phase due to its limiting solubility. The precipitated oligomeric radicals could then adsorb surfactant molecules as well as monomer to become micellar particles which served as sites for further polymerization (homogeneous nucleation). On the other hand, particle nucleation may also occur through direct capture of radicals/oligomeric radicals by fine emulsified monomer droplets (fine monomer droplets nucleation).

For iBMA emulsion polymerization, homogeneous nucleation was less likely to occur due to its low solubility in the aqueous phase (0.023 v/v %). However, micellar and fine monomer droplets nucleation mechanisms were quite likely for the iBMA emulsion system which used a relatively high CTAB content (1 to 6 wt%) to stabilize only 3 to 5 wt% iBMA. It is thus envisaged that a fraction of polymer particles would be produced via fine monomer-droplet nucleation for emulsion polymerization in addition to the micellar entry mechanism. This explains the low rate dependency on CTAB concentration (ca. 0.30) for emulsion polymerization for both monomers. It is well known that the rate dependency of 0.60 on the surfactant concentration should be observed for emulsion polymerization via micellar nucleation according to the Smith-Ewart theory (Case II) [24]. Although the likelihood for homogeneous nucleation in MMA emulsion polymerization cannot be ruled out, its contribution to polymerization is expected to be less significant than those of micellar entry and fine monomer droplets nucleation, since the rate dependencies on the surfactant concentration for the emulsion polymerization of both MMA and iBMA are similar.

In the case of microemulsions, almost all MMA and iBMA were present in the microemulsion droplets. Thus the principal loci of particle formation were in microemulsion droplets. This is because an extremely large surface area (large number of small microemulsion droplets) was available for capturing oligomeric radicals. The classical micellar nucleation mechanism is thus valid for the microemulsion polymerization of MMA and iBMA, and their rate dependencies on the surfactant concentrations are expected to be approximately 0.60. However, the situation is totally different for the microemulsion polymerization for a very low concentration of monomer. It was found that $(R_p)_i$ decreases with an increase of CTAB concentration (up to 10 wt%) for Series A and E which contained only 3 wt% of MMA and iBMA, respectively. The viscosities of these microemulsions at the polymerization temperature (60°C) were similar to those containing lesser surfactant concentrations. This excludes the effect due to the change of the micellar structures at different surfactant concentrations under this study. A similar inverse effect of the rate of microemulsion polymerization has also been reported by Shah et al. [5] and Donescu et al. [25], but no satisfactory explanation was given.

For those microemulsions containing a very low monomer concentration (3 wt%) but with a high surfactant concentration, they generate an enormous number of micelles which are slightly swollen by a small amount of monomer. The decreasing rate of microemulsion polymerization of this type might be simply attributed to the monomer dilution effect due to the increasing number of micelles. When radicals/oligomeric radicals begin polymerizing in these monomer-deficient microemulsion droplets, the limiting amount of monomer in the uninitiated microemulsion droplets is siphoned to the growing particles. As a result, many such microemulsion droplets become very deficient in monomer and are less likely to be active loci for polymerization. But these numerous monomer-deficient microemulsion droplets/micelles can still capture radicals without leading to a successful polymerization. The consequence of this is a lower rate of polymerization. The molecular weight of the polymer is also expected to be lower for Series A (Fig. 5) and E (Fig. 8) because of an insufficient supply of monomer to growing particles. However, the molecular weight of polymer was almost independent of CTAB concentration at a higher monomer concentration (>5 wt%) as shown by Series B and C of Fig. 5 and Series F of Fig. 8.

When the monomer concentration in a microemulsion was increased to a certain level, all microemulsion droplets became monomer-rich particles which were deemed to be potential loci for polymerization. The number of the potential loci for polymerization would be further increased with an increase of the surfactant concentration in a microemulsion polymerization system. Consequently, $(R_p)_i$ slightly increased again, as shown by Series C and D of Fig. 3 and Series F of Fig. 6.

As for the rate of polymerization which decreased in crossing the region between emulsion and microemulsion, it may be due to the gradual shift of particle-nucleation mechanisms. For MMA and iBMA, it is believed that besides micellar nucleation, fine monomer droplet nucleation might contribute significantly to the rate of emulsion polymerization because of weaker interfacial layers (less compact surfactant layer) of particles. On the other hand, the micellar mechanism prevails in microemulsion polymerization. However, the relatively rigid interfaces (more compact surfactant layers) at microemulsion droplets may slow down the rate of polymerization. Hence the decrease of $(R_p)_i$ in the boundary region between emulsion and microemulsion may imply that the micellar nucleation mechanism is increasingly dominant.

The exponential dependencies of N_d on CTAB concentration (Table 5) are much higher than the theoretical value of 0.60 found by the Smith-Ewart theory for the emulsion polymerization of styrene [24]. The high dependency may be attributed to radical desorption and continuous nucleation. Guo et al. [26] showed that the growing polymer radicals in microemulsion particles are readily terminated by chain transfer to monomer. The newly created monomeric radicals may then escape from the small particles to the aqueous phase and reenter particles needed for continuous nucleation. Owing to the easy escape of radicals from the smaller sized iBMA particles, their N_d dependency is much higher than that of the MMA system. Our present understanding of the high dependency of N_d on CTAB concentration is still very limited. The negative dependency of N_d for the MMA microemulsion system is believed to be due to the decrease of N_d arising from particle coalescence. This is because MMA also functions as a cosurfactant, but iBMA does not. The interfaces of PMMA particles in microemulsion would be rather fluid and sticky in collisions. At higher CTAB concentrations in microemulsions, more free counterions are available to screen the electrostatic repulsion among the positively charged head groups of CTAB. Such a reduction of surface potential of polymer particles favors particle coalescence.

CONCLUSION

The polymerizations of a relatively polar MMA and a less polar iBMA have been studied in a ternary-component system varying from a turbid emulsion to a transparent microemulsion. The initiation mechanism in the emulsion polymerization is quite different from that of microemulsion polymerization for both monomers. The former polymerization system may involve micellar, homogeneous, and fine monomer-droplet nucleations, but the principal loci of particle formation for the latter are in the microemulsion droplets. The rates of polymerization for both monomers decrease in crossing the transition region between emulsion and microemulsion due to a gradual shift of particle-nucleation mechanisms. The monomer concentration also affects the rate dependency on the surfactant concentration.

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