Particle nucleation loci in emulsion polymerization of methyl methacrylate

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Abstract

A water-insoluble dye was used as a probe to study the particle nucleation mechanisms in the semibatch emulsion polymerization of methyl methacrylate. The experimental results show that homogeneous nucleation plays a key role in the particle formation period. When the surfactant concentration ([S]) is above its critical micelle concentration (CMC), the mixed modes of particle nucleation (micellar and homogeneous nucleation) are operative in the polymerization system. In the absence of micelles, homogeneous nucleation is the predominant mechanism. Limited flocculation of latex particles becomes more important in controlling the particle concentration as the initiator concentration ([I]) is increased from 2.66 to 31.92 mM. When [S] is kept constant at 12 mM, the degree of formation of particle nuclei in the aqueous phase increases with increasing [I]. Monomer droplet nucleation, however, cannot be ruled out. This is because diffusion of dye molecules from monomer droplets to the growing latex particles originating from homogeneous nucleation is prohibited and in the absence of micelles an appreciable amount of dye still can be detected in the resultant latex particles. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion polymerization; Methyl methacrylate; Particle nucleation loci

1. Introduction

According to the micellar nucleation model [1–4], submicron latex particles are generated via capture of free radicals by the monomer-swollen micelles in emulsion polymerization. The emulsified monomer droplets are not effective in competing with micelles for the incoming radicals due to the relatively small total droplet surface area. Polymerization takes place primarily in the latex particles and monomer droplets only serve as a reservoir to supply the growing particles with monomer and surfactant. The number of latex particles per unit volume of water (N_p) is proportional to the surfactant concentration ([S]) and initiator concentration ([I]) to the 0.6 and 0.4 power, respectively. It should be noted that some mechanisms other than micellar nucleation must be responsible for the particle formation process when [S] is below the critical micelle concentration (CMC). By contrast, Priest [5] and Fitch and Tsai [6,7] proposed the homogeneous nucleation mechanism, in which free radicals generated in water become insoluble when a critical chain length is achieved. The water-insoluble

oligomeric radical may thus coil up and form a particle nuclei. This is followed by formation of stable primary particles via limited flocculation among the unstable particle nuclei and adsorption of surfactant species on their particle surfaces. The surfactant molecules required to stabilize these primary particles come from those dissolved in water and those adsorbed on the monomer droplet surfaces. The coagulative nucleation mechanism [8–10] suggests that the precursor particles are first generated by phase separation of the oligomeric radicals in the aqueous phase. These precursor particles, although completely covered with surfactant molecules, are extremely unstable and they aggregate rapidly until a stable (primary) particle size is achieved. The number of primary particles generated is controlled by the level of surfactant available for stabilizing the colloidal particles. Both the homogeneous and coagulative nucleation mechanisms emphasize the significance of polymerization occurring initially in the continuous aqueous phase. Monomer droplets generally do not contribute to particle nucleation to any appreciable extent. However, the homogenized submicron monomer droplets containing an extremely hydrophobic, low molecular weight compound such as hexadecane may

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Table 1
A typical recipe for the semibatch emulsion polymerization of methyl methacrylate at 80°C: $[S] = 12$ mM; $[I] = 6.3$ mM; and W(Dye) = 0.15%

	Chemicals	Weight (g)
Initial reactor charge	H_2O	160
	SDS	0.57
	$NaHCO_3$	0.037
Initial monomer charge	MMA	2
	Dye	0.06
Initiator solution	H_2O	5
	$Na_2S_2O_8$	0.25
Monomer feed	MMA	38

become the predominant particle nucleation loci (monomer droplet nucleation) [11,12].

To determine which mechanism predominates in the particle nucleation process is not straightforward. For example, Roe [13] showed that the fact that the experimental data follow the relationship $N_p \backsim [S]^{0.6}[I]^{0.4}$ does not necessarily confirm the Smith–Ewart theory. In our previous work [14], a water-insoluble blue dye was used as a probe for determining the particle nucleation loci in the semibatch emulsion polymerization of hydrophobic styrene (ST). Immediately before the start of polymerization, most of the dye species are present in the monomer droplets and some of them are solubilized in the monomer-swollen micelles. The extremely hydrophobic dye molecules cannot diffuse from the monomer droplets and micelles to the growing latex particles. Thus, determination of the amount of dye incorporated into the resultant latex particles provides valuable information on the particle nucleation mechanism. The semibatch polymerization technique was adopted to improve the measurement accuracy of the dye concentration in the latex particles. The experimental results clearly demonstrated the feasibility of using the water-insoluble dye to study the particle nucleation mechanisms involved. The mixed modes of particle nucleation (micellar and homogeneous nucleation) were proposed when $[S] >$ CMC. In the absence of micelles (i.e. $[S] <$ CMC), most of the latex particles are produced via homogeneous nucleation. The water solubility of methyl methacrylate (MMA) is 0.16 M, which is about 80 times as large as that of ST [15]. For the reaction system containing the relatively hydrophilic MMA, the aqueous phase polymerization and, hence, homogeneous nucleation are expected to be greatly enhanced. The objective of this work was therefore to employ the water-insoluble dye to study the particle nucleation mechanisms involved in the semibatch emulsion polymerization of MMA. Sodium dodecyl sulfate, sodium persulfate and sodium bicarbonate were used as the surfactant, initiator and buffer, respectively, in the reaction system.

2. Experimental

2.1. Materials

Methyl methacrylate (Kaohsiung Monomer Co.), sodium dodecyl sulfate (J.T. Baker), water-insoluble blue dye (Blue 70, Shenq-Fong Fine Chemical Ltd, China), sodium persulfate (Riedel-de Haen), sodium bicarbonate (Riedel-de Haen), acetone (Acros), nitrogen (Ching-Feng-Harng Co.), and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance < 0.057 μS/cm). Methyl methacrylate was distilled under reduced pressure before use. All other chemicals were used as received.

2.2. Polymerization process

Polymerization was carried out in a 250 ml reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. A typical recipe for the semibatch process is shown in Table 1. First, the initial reactor charge comprising H_2O, SDS and $NaHCO_3$ was charged into the reactor and then purged with N_2 for 10 min while the reactor temperature was brought to 80°C. This was followed by addition of a small amount of dye in MMA (initial monomer charge) to the reactor and the resultant monomer emulsion was subjected to mechanical agitation at 400 rpm for 30 min. The reaction was then initiated by the addition of the persulfate solution. Fifteen minutes after the start of polymerization, the remaining monomer in the absence of dye was fed to the reactor over a period of 90 min (feed rate = 0.42 g/min) by a FMI pump. After the monomer feed was complete, the reaction system was held at 80°C for 150 min to reduce the level of residual monomer. The weight percentage of dye based on total monomer (W(Dye)) was kept constant at 0.15% throughout this work. The polymerization temperature and agitation speed were kept constant at 80°C and 400 rpm, respectively, throughout the reaction. The theoretical solid content of the latex product is about 20%.

2.3. Characterization of latex products

The latex product was filtered through 40-mesh (0.42 mm) and 200-mesh (0.074 mm) screens in series to collect the filterable solids. Scraps adhering to the agitator, thermometer and reactor wall were also collected. Total solid content and conversion of ST (X) were determined by the gravimetric method. The latex particle size (d_p) was determined by dynamic light scattering (Otsuka Photal LPA-3000/3100). The sample was diluted with water to adjust the number of photons counted per second (cps) from 8000 to 12000. The reported d_p data represent an average of at least three measurements and the errors have been estimated to be about 3% for the polymerizations with $[S] =$ 1–20 mM and 10% for the ones with $[S] = 0.1$ mM.

A distinct peak at 670 nm was observed for the solution of 1.7×10^{-4} g blue dye and 0.2 g dried polymethyl

Table 2
Effect of surfactant concentration on the semibatch emulsion polymerization of methyl methacrylate at 80°C: $[I] = 6.3$ mM

[S] (mM)	X (%)	d_p (nm)	N_p/N_m	R_i/N_m (1/s)	$N_{p,m} \times 10^{-18}$ (1/L-H_2O)	$N_{p,h} \times 10^{-19}$ (1/L-H_2O)
0.1	80.9	211				
1	83.9	146				
2	82.5	103				
4	79.6	54				
6	81.4	32				
8	80.4	28				
10	81.9	23	2.14	0.055	4.789	2.803
12	82.1	22	1.26	0.026	5.553	3.501
14	81.7	20	0.97	0.017	9.302	3.836
16	81.9	19	0.85	0.013	9.908	4.601
18	82.0	18	0.82	0.010	9.605	5.815
20	80.5	17	0.80	0.0083	14.260	6.605

methacrylate in 20 ml acetone by UV absorbance (Shimadzu, UV-160A). However, no absorbance was detected at this wavelength for the solution of 0.2 g dried polymethyl methacrylate in 20 ml acetone. Thus, the presence of polymethyl methacrylate in the sample does not show any effect on the UV absorbance of the blue dye at 670 nm. The extinction coefficient of the calibration straight line established by a series of standards (2 g dye-free polymethyl methacrylate latex and a prescribed quantity of dye dissolved in 20 ml acetone) is 1.0033×10^5 ml/g cm. It has been shown that P_{dye} becomes insensitive to changes in sampling time when the sampling time is longer than 6 days for the ST emulsion polymerization [14]. Thus, the latex product was allowed to stand at room temperature for 12 days before determination of the amount of dye incorporated into the latex particles. In this manner, a thin layer of blue precipitate (originating from the bulk dye suspended in the latex product) can be found on the bottom of the sample. About 2 g sample was pipetted from the middle portion of the latex sample and then dried in an oven. Subsequently, the dried polymethyl methacrylate sample was dissolved in 20 ml acetone for P_{dye} measurement. The P_{dye} data reported in this work represent an average of five samples.

3. Results and discussion

3.1. Effect of surfactant concentration

First, the concentration of initiator ($[I]$) was kept constant at 6.3 mM and the concentration of surfactant ($[S]$) was varied from 0.1 to 20 mM. In this series, the average of the total scrap data is only $0.15 \pm 0.05\%$ based on total monomer. This level of coagulum indicates that the colloidal stability of the MMA emulsion polymerization with various levels of $[S]$ is quite satisfactory. The monomer conversion (X) and latex particle size (d_p) data, determined at the end of polymerization, are compiled in Table 2. The number of latex particles per unit volume of water (N_p) can be calculated according to the following mass balance

equations.

$$N_p = 6W_{m,t}/\{\pi d_p^3[\rho_m(1 - X) + \rho_p X]\} \quad \text{when } X > X_{II} \tag{1}$$

$$\pi/6d_p^3[\Phi_m\rho_m + (1 - \Phi_m)\rho_p]N_p = W_{m,t}X + W_{m,p} \tag{2a}$$

when $X \le X_{II}$

$$\Phi_m\rho_m/MW_m = [M]_p \tag{2b}$$

$$(W_{m,p}/MW_m)/[(W_{m,t}X/\rho_p) + (W_{m,p}/\rho_m)] = [M]_p \tag{2c}$$

where $W_{m,t}$ is the total monomer weight per unit volume of water shown in the recipe, ρ_m and ρ_p are the monomer density and polymer density, respectively, and MW_m is the molecular weight of monomer. X_{II} is the monomer conversion at which point monomer droplets disappear (i.e. the end of Smith–Ewart interval II). Φ_m, $W_{m,p}$ and $[M]_p$ are the volume fraction of monomer in the latex particles, the weight of monomer absorbed in the particles per unit volume of water, and the saturated monomer concentration in the latex particles, respectively, when $X \le X_{II}$. The parameters required for calculating N_p were determined in this study or obtained from literature (see Tables 2 and 3).

Fig. 1a shows the log N_p vs. log $[S]$ data. When $[S] >$ CMC (8.2 mM), the slope obtained from the least squares

Table 3
Kinetic parameters for the emulsion polymerization of styrene at 80°C

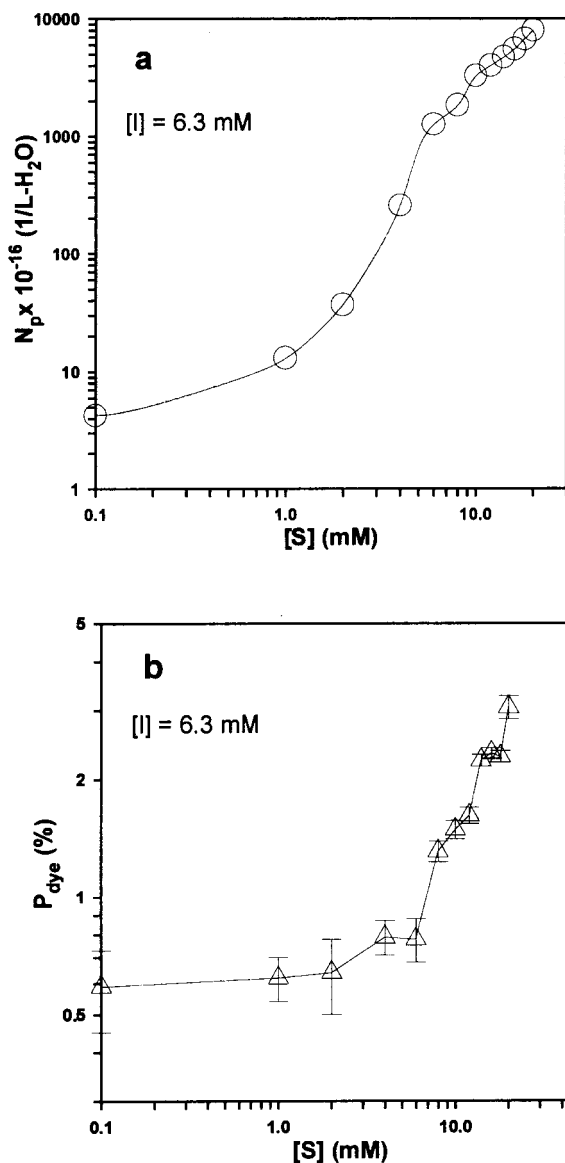| Parameter	Numeric value	Units	References
CMC	8.2	mM	[16]
M	71		[17,18]
F	1		
k_d	1.10×10^{-4}	1/s	[19]
ρ_m	0.94	g/ml	
ρ_p	1.19	g/ml	
X_{II}	42.9%		[20]
$[M]_p$	5.9	mol/l	[20]

Fig. 1. (a) Final number of latex particles per unit volume of water as a function of the surfactant concentration (slope = 1.28 when $[S] >$ CMC and slope = 1.27 when $[S] <$ CMC) and (b) weight percentage of dye incorporated into the final latex particles as a function of the surfactant concentration (slope = 0.97 when $[S] >$ CMC and slope = 0.07 when $[S] >$ CMC) : $[I] = 6.3$ mM.
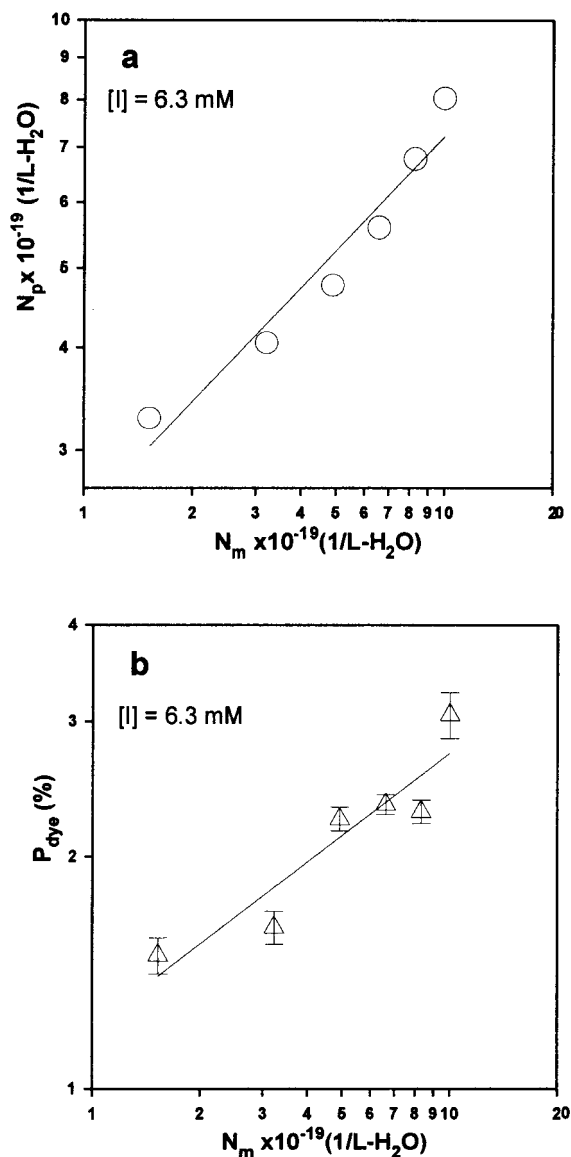

Fig. 2. (a) Final number of latex particles per unit volume of water as a function of the number of micelles per unit volume of water (slope = 0.46) and (b) weight percentage of dye incorporated into the final latex particles as a function of the number of micelles per unit volume of water (slope = 0.35) : $[I] = 6.3$ mM.

best fitted log N_p vs. log $[S]$ straight line is 1.28, which is much higher than the theoretical value (0.6) derived for the batch emulsion polymerization that obeys the micellar nucleation model. The difference in the dependence of N_p on $[S]$ is attributed to the deviation from the micellar nucleation model and/or the semibatch process used in this work. Above the CMC, P_{dye} is proportional to $[S]$ to the 0.97 power, which is smaller than that obtained from the log N_p vs. log $[S]$ data (1.28). The number of micelles per unit volume of water (N_m) formed just before the start of polymerization can be estimated by the following equation provided that the

influence of monomer and dye is insignificant.

$$N_m = ([S] - \text{CMC})/m \qquad (3)$$

where m is the number of SDS molecules in one micelle (i.e. aggregation number). The values of CMC and m for the aqueous SDS solution can be found in Table 3. Fig. 2 shows that the slope obtained from the least squares best fitted log N_p vs. log N_m straight line (0.46) is greater than that obtained from the log P_{dye} vs. log N_m data (0.35). This result indicates that N_p increases more rapidly than P_{dye} does when N_m increases from 1.53×10^{19} to 1.00×10^{20} 1/L-H$_2$O. When $[S] >$ CMC, the difference in the dependence of N_p and P_{dye} on N_m implies that some mechanisms other than
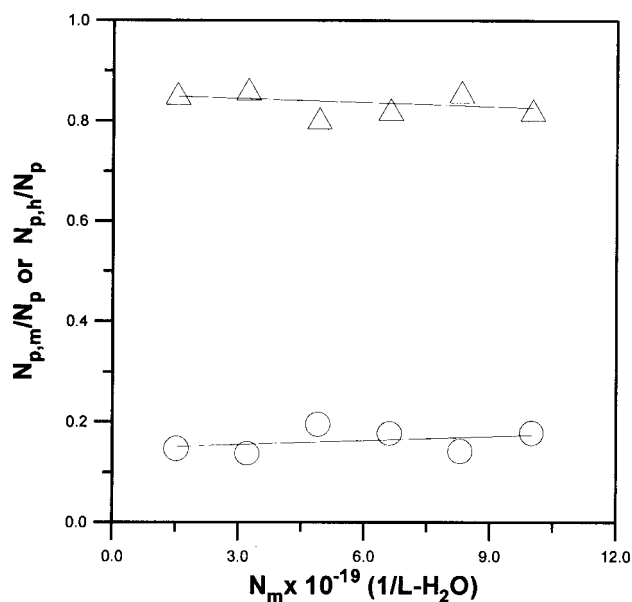
Fig. 3. Fraction of latex particles originating from micellar nucleation ($N_{p,m}/N_p$, ○) and fraction of latex particles originating from homogeneous nucleation ($N_{p,h}/N_p$, △) as a function of the number of micelles per unit volume of water: $[I] = 6.3$ mM.

micellar nucleation must have been operative in the particle formation process.

The above postulation is further supported by the N_p/N_m and R_i/N_m data in Table 2. N_p/N_m represents the fraction of micelles which can be successfully transformed into latex particles if micellar nucleation predominates in the particle formation period. R_i/N_m represents the number of free radicals captured per second by one micelle, in which $R_i = 2fk_d[I]$ is the generation rate of free radicals in water, f the initiation efficiency factor, and k_d the initiator decomposition rate constant. The parameters f and k_d required for calculating R_i are listed in Table 3. R_i/N_m decreases significantly with increasing $[S]$. This trend leads to the conclusion that the probability of capturing free radicals by micelles decreases with increasing N_m. Thus, the higher the concentration of micelles, the smaller is the fraction of micelles, which can be successfully converted into latex particles. This inference is further supported by the N_p/N_m data shown in Table 2. That is, N_p/N_m decreases significantly when $[S]$ increases from 10 to 20 mM (or N_m increases from 1.53×10^{19} to 1.00×10^{20} 1/L-H$_2$O). However, not all the latex particles originate from micellar nucleation. This is because an abundant supply of SDS molecules in the unnucleated micelles is available for stabilizing the primary particles generated in the aqueous phase via homogeneous nucleation. For example, $N_p/N_m = 2.14$ for the polymerization system with $[S] = 10$ mM suggests that at least $(2.14 - 1)/2.14 \times 100\% = 53\%$ of the resultant latex particles are produced by homogeneous nucleation (see Table 2). As a matter of fact, it will be shown later that about 85% of latex particles originates from homogeneous

nucleation for the polymerization system with $[S] = 10$ mM (see the $N_{p,m}$ and $N_{p,h}$ data in Table 2 and Fig. 3). The particle nuclei just formed in the aqueous phase and the growing latex particles may compete effectively with micelles for free radicals and SDS molecules. Such a competitive process may result in a reduction in the importance of micelles in the particle nucleation period. The concentration of latex particles originating from homogeneous nucleation should increase with increasing $[S]$. This is due to the fact that more micelles do not contribute to formation of latex particles and they only serve as a reservoir to provide the growing latex particles and particle nuclei generated in water with monomer and SDS. Therefore, the rate of increase in P_{dye} is slower than the rate of increase in N_p with $[S]$. In other words, the slope obtained from the least squares best fitted log P_{dye} vs. log N_m straight line (0.35) is smaller than that obtained from the log N_p vs. log N_m data (0.46). In summary, the mixed modes of particle nucleation (micellar and homogeneous nucleation) are operative in the semibatch emulsion polymerization of MMA in the presence of micelles.

Chern and Lin [14] defined $P_{dye,m}$ as the percentage of the added dye initially solubilized in the micelles and $N_{p,m} = N_m(P_{dye} - P_{dye,0})/P_{dye,m}$ and $N_{p,h} = N_p - N_{p,m}$ then represent the number of latex particles per unit volume of water originating from micellar nucleation and homogeneous nucleation, respectively. Since the value of $P_{dye,m}$ for MMA in the aqueous SDS solution is not available, as a first approximation, the solubilization data for the benzene/SDS/H$_2$O system (about 1.7 mol benzene per mol SDS solubilized in the SDS micelles) was used to estimate $P_{dye,m}$ [21]. For example, for the recipe shown in Table 1, the reactor system consists of 165 g H$_2$O, 2 g MMA, 0.57 g SDS (12 mM based on water), 0.037 g NaHCO$_3$, 0.25 g Na$_2$S$_2$O$_8$, and 0.060 g dye immediately before the start of polymerization. The amounts of MMA and dye which can be solubilized in the micelles are $1.7 \times (12 - 8.2) \times 10^{-3} \times (165/1000) \times 100 = 0.107$ g MMA and $0.060 \times 0.107/2 = 0.0032$ g dye, respectively. The numeric values of 8.2 (mM) and 100 (g/mol) are the CMC of the aqueous SDS solution (see Table 3) and the molecular weight of MMA, respectively. Thus, $P_{dye,m} = 0.0032/0.06 \times 100\% = 5.33\%$. $P_{dye,0}$ (0.7%, see the P_{dye} vs. $[S]$ data in Fig. 1a) is the average of the P_{dye} data for the polymerizations with $[S] = 0.1–6$ mM (i.e. in the absence of micelles). $P_{dye,0}$ is simply used as the blank in the above mass balance equations. Table 2 shows that both $N_{p,m}$ and $N_{p,h}$ increase with increasing $[S]$ (or N_m). This is because more micelles can participate in the particle nucleation process and more surfactant molecules are available for stabilizing the particle nuclei born in the aqueous phase when $[S]$ increases from 8 to 20 mM. Furthermore, Fig. 3 shows that $N_{p,m}/N_p$ is always smaller than $N_{p,h}/N_p$ at constant N_m and both $N_{p,m}/N_p$ and $N_{p,h}/N_p$ are relatively insensitive to changes in N_m. This result indicates that homogeneous nucleation plays a key role in the semibatch emulsion polymerization of relatively

Table 4
Effect of initiator concentration on the semibatch emulsion polymerization of methyl methacrylate at 80°C

$[S]$ (mM)	12	12	12	12	12	12	12	4	4	4	4	4	4
$[I]$ (mM)	2.66	5.32	6.30	8.00	13.30	21.28	31.92	2.66	5.32	6.30	13.30	21.28	31.92
X (%)	82.9	84.2	82.1	84.4	86.4	83.4	84.5	82.3	85.8	79.6	80.5	85.7	85.8
d_p (nm)	25	23	22	24	38	56	38	67	65	54	56	156	228
R_i/N_m (1/s)	0.011	0.022	0.026	0.033	0.055	0.087	0.13						

hydrophilic MMA. However, the population of latex particles originating from micellar nucleation ($N_{p,m}/N_p =$ ca 0.16) cannot be ignored. Note that the $N_{p,m}$ and $N_{p,h}$ data are by no means accurate since the solubility parameter of MMA (8.8 (cal/cm^3)$^{1/2}$) is different from that of benzene (9.2 (cal/cm^3)$^{1/2}$) [22], thereby leading to the different extent
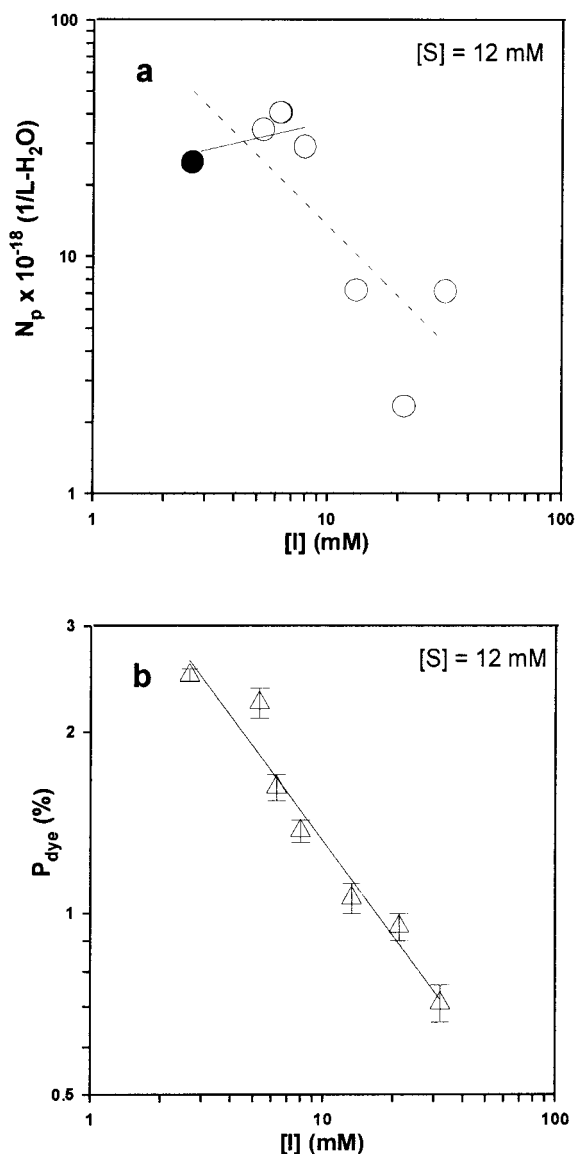

Fig. 4. (a) Final number of latex particles per unit volume of water as a function of the initiator concentration (slope = 0.23 for the solid line and slope = −0.99 for the dashed line) and (b) weight percentage of dye incorporated into the final latex particles as a function of the initiator concentration (slope = −0.52) : $[S]$ = 12 mM.

to which MMA can be incorporated into the SDS micelles. In addition, the influence of the solubilization of dye and MMA in the micelles and the presence of monomer droplets on the values of CMC and m is not known. All these factors may result in erroneous estimation of $P_{dye,m}$. Thus, these $N_{p,m}$ and $N_{p,h}$ data only provide one with qualitative information on the competitive micellar and homogeneous nucleation mechanisms.

Below the CMC of the aqueous SDS solution, Fig. 1a shows that N_p first increases gradually and then rises rapidly with increasing $[S]$. This is simply because more surfactant molecules are available for stabilizing the primary particles generated in the aqueous phase when $[S]$ increases from 0.1 to 6 mM. Although the N_p vs. $[S]$ data do not exhibit a linear relationship for the polymerization system with $[S] =$ 0.1–6 mM, the slope obtained from the least squares best fitted straight line is 1.27 (i.e. $N_p \backsim [S]^{1.27}$). On the contrary, Fig. 1b shows that P_{dye} is relatively insensitive to changes in $[S]$ and the relationship $P_{dye} \backsim [S]^{0.07}$ holds when $[S] <$ CMC. This result implies that, in the absence of micelles, most of the latex particles are generated by homogeneous nucleation. The average of the P_{dye} data is 0.7% and the dye species incorporated into the latex particles cannot be attributed to formation of particle nuclei in the aqueous phase because the extremely hydrophobic dye is incapable of diffusing from monomer droplets to the aqueous phase. It is then postulated that nucleation in a small fraction of the dye containing monomer droplets (ca 0.7%) may take place in the course of polymerization. Therefore, an appreciable amount of dye was detected in the resultant latex particles. Another possible explanation is that collision between the latex particles and monomer droplets by shear force may promote transport of dye/ST from monomer droplets to latex particles. Furthermore, both the concentrations of latex particles and monomer droplets increase with increasing $[S]$ and this will enhance the frequency of collision between the latex particles and monomer droplets. As a result, P_{dye} increases gradually when $[S]$ increases from 0.1 to 6 mM ($P_{dye} \backsim [S]^{0.07}$, see Fig. 1b). Nevertheless, formation of particle nuclei in water should predominate in the particle nucleation period when $[S] <$ CMC. This is because the concentration of monomer droplets initially present in the reaction system is much lower than that of latex particles produced.

3.2. Effect of initiator concentration
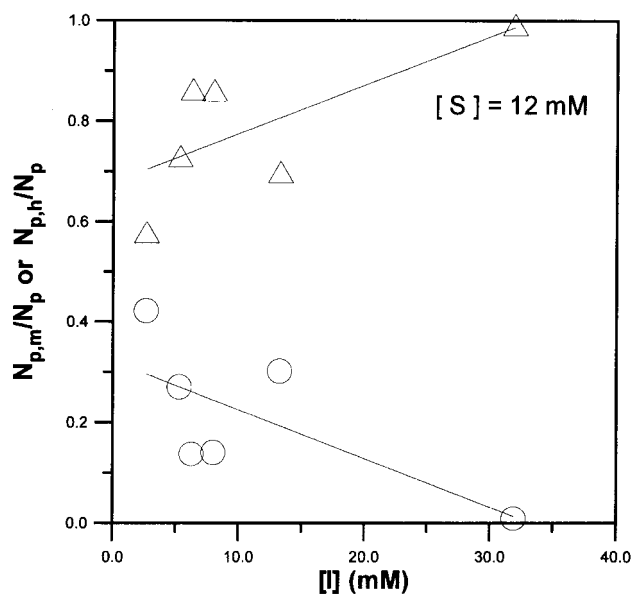
In this section, $[S]$ was kept constant at 12 or 4 mM,

Fig. 5. Fraction of latex particles originating from micellar nucleation ($N_{p,m}/N_p$, ○) and fraction of latex particles originating from homogeneous nucleation ($N_{p,h}/N_p$, △) as a function of the initiator concentration: $[S] = 12$ mM.

whereas $[I]$ was varied from 2.66 to 31.92 mM. The X and d_p data are summarized in Table 4. Fig. 4 shows the data of log N_p and log P_{dye} as a function of log $[I]$ for the polymerization system with $[S]$ (12 mM) > CMC. Without taking into account the closed cirular data points in Fig. 4a, the slope obtained from the least squares best fitted log N_p vs. log $[I]$ straight line is 0.23 ($[I] = 2.66$–8.00 mM, see the dashed line in Fig. 4a). On the other hand, the relationship $N_p \frown [I]^{-0.99}$ holds when all the data points in Fig. 4a are used in the regression procedure ($[I] = 2.66$–31.92 mM, see the solid line in Fig. 4a). It is very difficult to judge which correlation is correct, but changes in the colloidal stability of latex particles with $[I]$ might be responsible for the complicated dependence of N_p on $[I]$. The ionic strength of the aqueous solution increases with increasing $[I]$. According to DLVO theory [23,24], the increased ionic strength will compress the electric double layer around the latex particles and, thereby, reduce the electrostatic potential energy barrier against flocculation (i.e. the colloidal stability of latex particles). Nevertheless, the average of the total scrap data for this series of experiments is only $0.08 \pm 0.04\%$, which is comparable to that of the surfactant concentration series (total scrap = $0.08 \pm 0.02\%$ for the polymerization system with $[I] = 6.3$ mM and $[S] = 8$–20 mM). Intensive coagulation among the interactive latex particles, which produces particle aggregates with dimension much larger than $1\ \mu$, is thus insignificant. It is then speculated that limited flocculation of latex particles must have occurred for the reaction system containing relatively high electrolyte concentration. Accompanying flocculation, the particle–water interfacial area decreases and the particle surface charge density increases, accordingly.

Under such circumstances, the flocculated latex particles may become stable again and formation of large flocs is prohibited (termed the limited flocculation process).

At low $[I]$ (2.66–8 mM), the electrolyte concentration is not high enough to induce flocculation of latex particles during polymerization. However, the probability of capturing free radicals by micelles is expected to increase with increasing $[I]$ (see the R_i/N_m data in Table 4). This will lead to the increased N_p with $[I]$ ($N_p \frown [I]^{0.23}$). By contrast, limited flocculation comes into play when $[I]$ increases from 8 to 31.92 mM. As a result, N_p decreases significantly with increasing $[I]$ (see Fig. 4a). It is interesting to note that P_{dye} decreases as $[I]$ is increased from 2.66 to 31.92 mM (see Fig. 4b). The slope obtained from the least squares best-fitted log P_{dye} vs. log $[I]$ straight line is -0.52. P_{dye} is expected to increase with increasing $[I]$. This is because the generation rate of free radicals in the aqueous phase ($R_i = 2fk_d[I]$) increases with increasing $[I]$. At constant $[S]$, the increased R_i enhances the probability of capturing free radicals by micelles (see the R_i/N_m data in Table 4). This may thus result in an increase in P_{dye} with $[I]$. However, the experimental data of log P_{dye} as a function of log $[I]$ show an opposite trend and this behavior is very difficult to explain. It is speculated that the degree of formation of particle nuclei via homogeneous nucleation increases with increasing $[I]$. In addition, monomer droplets are not the primary particle nucleation loci due to the keen competition provided by the very high concentration of micelles and particle nuclei produced in the aqueous phase. Generation of latex particles by homogeneous nucleation does not contribute to incorporation of dye into the latex particles because diffusion of the extremely hydrophobic dye species from monomer droplets to the latex particles generated in water is completely prohibited. As a result, the amount of dye incorporated into the latex particles decreases significantly with increasing $[I]$. This postulation is further supported by the data of $N_{p,m}/N_p$ and $N_{p,h}/N_p$ as a function of $[I]$ shown in Fig. 5. Although the data are somewhat scattered, $N_{p,h}/N_p$ is always greater than $N_{p,m}/N_p$ when $[I]$ is kept constant. $N_{p,h}/N_p$ increases and $N_{p,m}/N_p$ decreases when $[I]$ increases from 2.66 to 31.92 mM. This result clearly indicates that the higher the initiator concentration, the more important is the homogeneous nucleation mechanism in determining the concentration of latex particles produced.

The X and d_p data for the polymerizations with $[S]$ (4 mM) < CMC are also listed in Table 4. The data of log N_p and log P_{dye} as a function of $[I]$ are shown in Fig. 6. In the absence of micelles, the profile of the N_p vs. $[I]$ data is quite similar to the series of experiments with $[S] = 12$ mM (see Figs. 4a and 6a). Interesting enough, the log P_{dye} vs. log $[I]$ data for the polymerization system with $[S] = 4$ mM show an opposite trend in comparison with those data obtained from the experiments with $[S] = 12$ mM (see Figs. 4b and 6b). There is no doubt that homogeneous nucleation plays an important role in the polymerization system in the
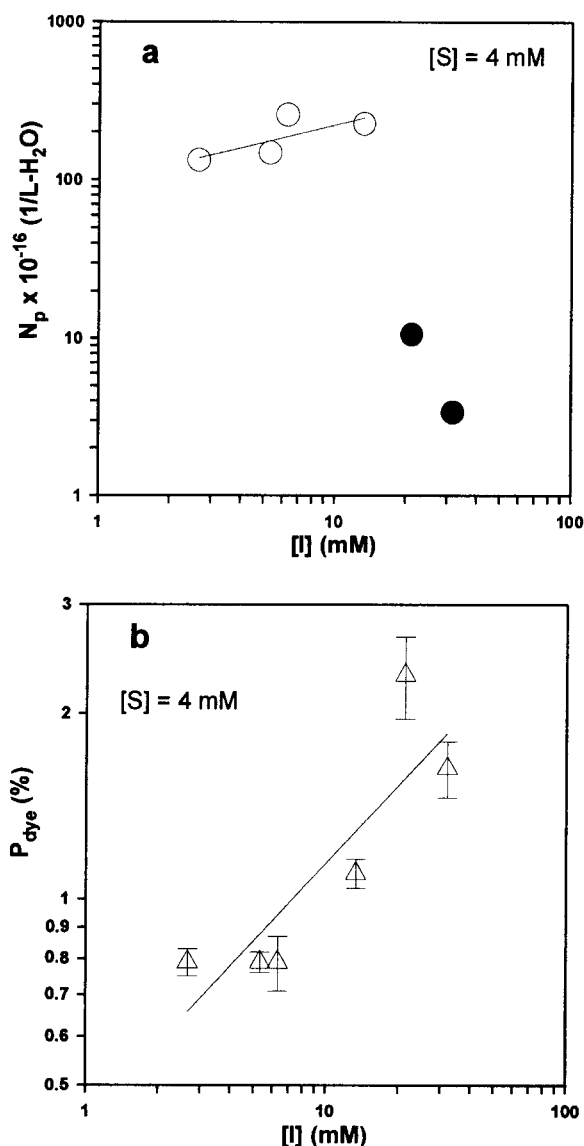
also promote transport of dye species from monomer droplets to latex particles and then result in an increase in P_{dye} with $[I]$.

4. Conclusions

Based on the data of the number of latex particles per unit volume of water (N_p) and the weight percentage of dye ultimately incorporated into latex particles (P_{dye}), the mixed modes of particle nucleation (micellar and homogeneous nucleation) are proposed for the semibatch emulsion polymerization of methyl methacrylate (MMA) when the surfactant concentration ($[S]$) is above its critical micelle concentration (CMC). Nevertheless, the fraction of latex particles originating from micellar nucleation ($N_{p,m}/N_p =$ ca 16%) is much smaller than the fraction of latex particles originating from homogeneous nucleation ($N_{p,h}/N_p =$ ca 84%). This result strongly suggests that homogeneous nucleation predominates in the particle formation process. In the absence of micelles ($[S] <$ CMC), most of the latex particles are produced via homogeneous nucleation. However, monomer droplet nucleation cannot be ruled out because an appreciable amount of dye can be detected in the resultant latex particles ($P_{dye} \backsim 0.7\%$).

For the polymerizations with $[S]$ (12 mM) $>$ CMC and the initiator concentration ($[I]$) = 2.66–8 mM, limited flocculation of latex particles is insignificant, but the probability of capturing free radicals by micelles increases with increasing $[I]$. This reaction mechanism is consistent with the relationship $N_p \backsim [I]^{0.23}$ established in this work. By contrast, limited flocculation becomes very important when $[I]$ increases from 8 to 31.92 mM. As a result, N_p decreases significantly with increasing $[I]$. The decreased P_{dye} with $[I]$ leads to the postulation that the concentration of latex particles generated by homogeneous nucleation increases significantly with increasing $[I]$, which is further supported by the data of $N_{p,m}/N_p$ and $N_{p,h}/N_p$. For the polymerizations with $[S]$ (4 mM) $<$ CMC, formation of particle nuclei in the aqueous phase plays an important role in the reaction system (homogeneous nucleation). Both the nucleation occurring in the dye containing monomer droplets and collision between the latex particles and monomer droplets (i.e. transport of dye molecules from monomer droplets to latex particles) increase with increasing $[I]$, thereby leading to the increased P_{dye} with $[I]$.

Acknowledgements

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Fig. 6. (a) Final number of latex particles per unit volume of water as a function of the initiator concentration (slope = 0.37 for the solid line) and (b) weight percentage of dye incorporated into the final latex particles as a function of the initiator concentration (slope = 0.42) : $[S]$ = 4 mM.

absence of micelles. However, monomer droplet nucleation cannot be ruled out. This is because P_{dye} also increases from 0.8 to 1.6% when $[I]$ increases from 2.66 to 31.92 mM and the relationship $P_{dye} \backsim [I]^{0.42}$ holds in this case (see Fig. 6b). The higher the initiator concentration, the faster is the generation rate of free radicals in the aqueous phase. The enhanced free radical concentration in water then increases the probability of capturing oligomeric radicals by the dye containing monomer droplets, thereby leading to an increase in P_{dye} with $[I]$. Furthermore, the electrolyte concentration will also increase with increasing $[I]$. Increasing the ionic strength will compress the electric double layer around the latex particles and, thereby, increase the frequency of collision (induced by the mechanical agitation) between the latex particles and monomer droplets. This factor may

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