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Using a water-insoluble dye to probe the particle nucleation loci in styrene emulsion polymerization

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Abstract

A water-insoluble dye was used to probe the particle nucleation loci in the semibatch emulsion polymerization of styrene (ST). Most of the dye molecules 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 mixed modes of particle nucleation (micellar and homogeneous nucleation) were proposed when the surfactant concentration ([S]) is above its critical micelle concentration (CMC). In the absence of micelles (i.e., [S] < CMC) most of the latex particles are produced via homogeneous nucleation. Monomer droplet nucleation cannot be ruled out because an appreciable amount of dye still can be detected in the resultant latex particles. The influence of the initiator concentration on the particle nucleation mechanisms was also investigated. The experimental data, again, support the proposed mixed modes of particle nucleation when [S] > CMC. Homogeneous nucleation plays an important role in the particle formation period when [S] < CMC. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion polymerization; Styrene; Particle nucleation loci

1. Introduction

Conventional emulsion polymerization is a process involving dispersion of a hydrophobic monomer such as styrene (ST) in water by using an oil-in-water surfactant such as sodium dodecyl sulfate (SDS). This is followed by addition of a persulfate initiator to start the reaction. The resultant latex products comprise a large number of submicron polymer particles (50–1000 nm in diameter) stably dispersed in water. Although the particle nucleation period is quite short (ca. 0–20% monomer conversion), it plays a key role in determining the resultant latex particle size (d_p) and particle size distribution. Control of the particle size and particle size distribution has a significant influence on the quality of latex products. Thus, to gain a better understanding of the particle nucleation mechanisms has been a central problem in emulsion polymerization since the 1940s.

The well known Smith–Ewart theory [1–3] proposes that latex particles are nucleated via capture of the relatively hydrophobic oligomeric radicals in water by the monomer-swollen micelles ($\sim 10^1$ nm in diameter, 10^{20}–10^{21} micelles per liter water). The probability of transforming the monomer droplets ($> 10^3$ nm in diameter, 10^{13}–10^{14} monomer droplets per liter water) into latex particles is slim due to the much smaller droplet surface area in comparison with micelles. Thus, these monomer droplets cannot compete effectively with micelles for the incoming oligomeric radicals, and they only serve the growing latex particles with monomer and surfactant during polymerization. The number of latex particles nucleated (N_p) is proportional to the surfactant concentration ([S]) and initiator concentration ([I]) to the 0.6 and 0.4 power, respectively. The remainder of the reaction is simply the growth of these latex particles via polymerization of the imbibed monomer provided by the monomer droplets. Note that the presence of micelles is a prerequisite for micellar nucleation to occur, that is, [S] must be above its critical micelle concentration (CMC). Thus, for the polymerization with [S] < CMC the latex particles must be generated by some mechanisms other than micellar nucleation. In addition, the micellar nucleation mechanism was criticized by Roe [4], who showed that the Smith–Ewart relationship $N_p \sim [S]^{0.6}[I]^{0.4}$ also can be derived without resort to the assumption of micellar nucleation. As a consequence, the fact that the experimental data obtained from a batch emulsion polymerization follow the

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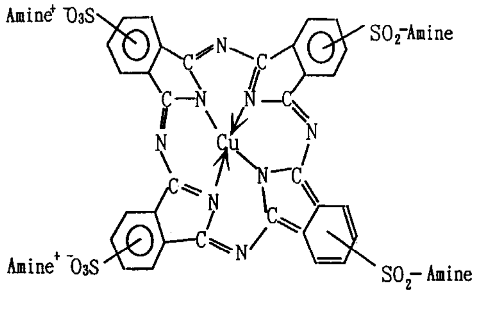

Scheme 1.

Table 1
A typical recipe for the semibatch emulsion polymerization of styrene 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	ST	2
	Dye	0.060
Initiator solution	H_2O	5
	$Na_2S_2O_8$	0.25
Monomer feed	ST	38

above relationship does not necessarily confirm the Smith–Ewart theory.

In contrast to micellar nucleation, Priest [5] and Fitch and Tsai [6,7] proposed that oligomeric radicals generated in water become insoluble when a critical chain length is achieved. This water-insoluble radical may thus coil up and form a particle nuclei ($\sim 10^0$ nm in diameter). Subsequently, stable primary particles ($\sim 10^1$ nm in diameter) are produced via limited flocculation among the unstable particle nuclei and adsorption of surfactant molecules on their particle surfaces. The surfactant species required to stabilize these primary particles come from those dissolved in water and those adsorbed on the monomer droplet surfaces. This particle formation process has been termed the homogeneous nucleation mechanism. Another interesting mechanism which also emphasizes the importance of the polymerization taking place initially in the aqueous phase is the two-step coagulative nucleation mechanism [8–10]. The precursor particles ($\sim 10^0$ nm in diameter) are first formed 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 (*ca.* 20–50 nm in diameter) is achieved. The number of primary particles nucleated is controlled by the amount of surfactant available for stabilizing the generated interfacial area. As mentioned above, monomer droplets with a diameter of 10^3 nm or larger do not contribute to nucleation of latex particles to any appreciable extent. Nevertheless, the homogenized monomer droplets containing an extremely hydrophobic, low-molecular weight compound, such as hexadecane, may become the predominant particle nucleation loci and this technique has been termed miniemulsion polymerization [11,12].

In our previous work [13,14], a water-insoluble blue dye (molecular weight $\sim 1 \times 10^3$ g/mol) was used as a probe for determining the particle nucleation loci in the ST miniemulsion polymerization. The structure of the dye molecule is shown in Scheme 1. Furthermore, the authors conducted a conventional emulsion polymerization in which a small amount of dye was added to the reaction mixture at a monomer conversion of 32.4%. The polymerization was then allowed to proceed to completion. The experimental data show that transport of the dye species from the bulk phase, across the aqueous phase, and then into the latex particles, is insignificant due to the very low water solubility of dye [13]. This result implies that the blue dye may be used as a probe to study the validity of the micellar nucleation mechanism, which has been generally accepted for the conventional emulsion polymerization of relatively water-insoluble monomers such as ST. The rationale behind this idea is briefly described as follows.

Nagarajan et al. [15] reported that about 1.7 mol of benzene (which has a similar molecular structure to ST) per mole SDS can be solubilized in the SDS micelles. For example, for the recipe comprising 165 g H_2O, 40 g ST, 0.57 g SDS (12 mM based on water), 0.037 g $NaHCO_3$, 0.25 g $Na_2S_2O_8$, and 0.060 g dye, the amounts of ST and dye which can be solubilized in the micelles are, as a first approximation, $1.7 \times (12-8.2) \times 10^{-3} \times (165/1000) \times 104 = 0.111$ g ST and $0.060 \times 0.111/40 = 0.000167$ g dye, respectively. Note that this example is a batch version of the recipe for the semibatch ST emulsion polymerization shown in Table 1. The numeric values of 8.2 (mM) and 104 (g/mol) are the CMC of the aqueous SDS solution (see Table 3) and the molecular weight of ST, respectively. Thus, when a small amount of dye in ST is dispersed in an aqueous SDS solution, about 99.72% of the added dye is distributed among the monomer droplets, and only 0.28% solubilized in the monomer-swollen micelles. If these micelles are the primary loci for nucleation, then the weight percentage of dye ultimately incorporated into the latex particles (P_{dye}) cannot be very high because the extremely hydrophobic dye molecules are incapable of diffusing from the monomer droplets to the latex particles during polymerization. After particle nucleation is complete, the latex particles continue to grow by absorption of monomer provided by the monomer droplets and/or the remaining monomer-swollen micelles. The surfactant species required to stabilize the expanding particle–water interfacial area come from those desorbed from the monomer droplets and un-nucleated micelles. As a result, the dye molecules originally present in the monomer droplets and un-nucleated micelles may become suspended as a bulk material in the aqueous phase towards the end of polymerization. Moreover, the Smith–Ewart relationship should be reflected in the P_{dye} versus [S] or [I] data provided that only micellar nucleation is operative in the production of latex particles. However, one problem of applying this method to batch emulsion polymerization is the rather limited quantity of dye which can be incorporated into the resultant latex particles. This may cause significant errors in the P_{dye} measurements (UV absorbance method). To alleviate this problem, a semibatch process was adopted in this work and a typical recipe is shown in Table 1. This semibatch process simply involves dispersion of 2 g ST in combination with 0.060 g dye in an aqueous SDS solution (12 mM), followed by polymerization at 80°C over a period of 15 min. The remaining monomer (38 g ST) in the absence of dye was then fed to the reactor over a period of 90 min primarily to support the propagation reaction taking place in the latex particles. Under the circumstances, the weight percentage of the added dye solubilized in the monomer-swollen micelles increases rapidly from 0.28% to 5.55% ((0.111/2) × 100%). The accuracy of using the water-insoluble dye to probe the particle nucleation loci may thus be greatly enhanced.

2. Experimental

2.1. Materials

The chemicals used in this work include styrene (Taiwan Styrene 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), toluene (Acros), nitrogen (Ching-Feng-Harng Co.) and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance $< 0.057\ \mu S/cm$). Styrene 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 $NaHCO_3$ (a buffer reagent) 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 ST (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 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 approximate 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 were determined by the gravimetric method. The resultant latex particle size (d_p) was determined by the dynamic light scattering method (Otsuka Photal LPA-3000/3100). The sample was diluted with water to adjust the number of photons counted per second (cps) to 8000–12 000. 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 experiments with [S] = 1–50 mM and 10% for the ones with [S] = 0.1 mM.

A distinct peak at 678 nm was observed for the solution of 1.7×10^{-4} g blue dye and 0.2 g dried polystyrene in 20 ml toluene by the UV absorbance method (Shimadzu, UV-160A). However, no absorbance was detected at this wavelength for the solution of 0.2 g dried polystyrene in 20 ml toluene. Thus, the presence of polystyrene in the sample does not show any effect on the UV absorbance of the blue dye at 678 nm. The calibration equation generated by least-squares best-fitting the UV absorbance at 678 nm versus the dye concentration ([dye]) data is: absorbance = 6.9368×10^4 [dye] (g/ml) + 1.6308×10^{-2} with the coefficient of determination (R^2) = 0.9981. To determine the amount of dye incorporated into the latex particles, the latex product was allowed to stand at room temperature over a prescribed period of time before UV absorbance measurements. 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. Approximate 2 g of sample was pipetted from the middle portion of the latex sample and then dried in an oven. Subsequently, the dried polymer particles were dissolved in 20 ml toluene for determination of P_{dye} according to the above calibration curve. The reported P_{dye} data represent an average of five samples.

3. Results and discussion

Fig. 1 shows the P_{dye} data as a function of sampling time for the polymerization with [S] = 6.0 mM and [I] = 6.3 mM. It is shown that P_{dye} becomes insensitive to changes in sampling time when the sampling time is longer than 6 days. Thus, in the remainder of this work the latex

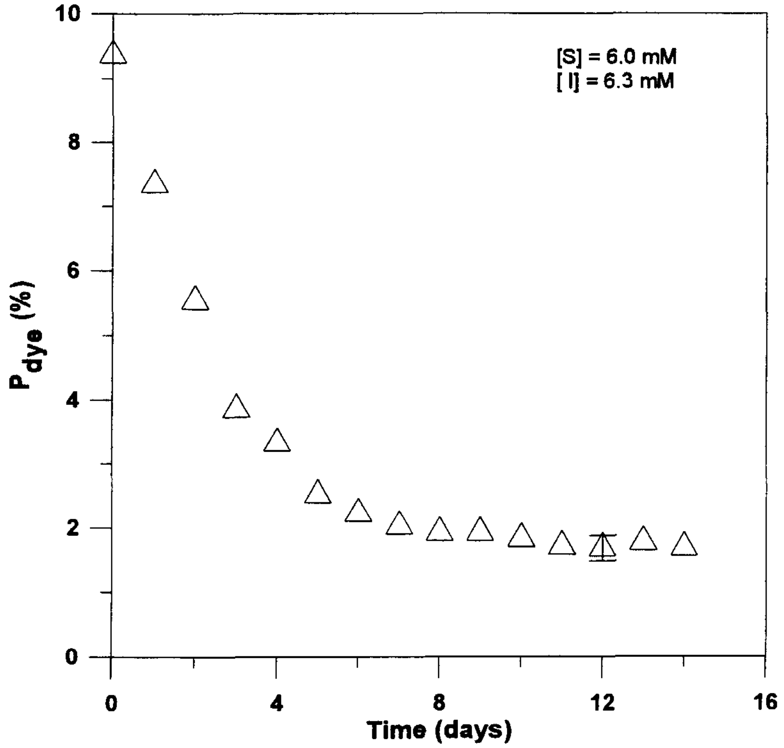

Fig. 1. Weight percentage of dye incorporated into the resultant latex particles as a function of sampling time.

products were allowed to stand at room temperature for 12 days before UV absorbance measurements.

3.1. Effect of surfactant concentration

In this series of experiments, [I] was kept constant at 6.3 mM, whereas [S] was varied from 0.1 to 50 mM. The average of the total scrap data is 0.6% based on total monomer for this series of experiments and this result indicates that the colloidal stability of the recipe with various levels of [S] used in this work is quite satisfactory. The monomer conversion (X) and latex particle size (d_p) data, determined at the end of polymerization, are summarized in Table 2. The number of latex particles generated per unit volume of water (N_p) can be calculated according to the following mass balance equations.

Table 2
Effect of surfactant concentration on the semibatch emulsion polymerization of styrene 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)	$N_{p,h} \times 10^{-18}$ (1/L-H_2O)
0.1	33.2	448.0				
1	38.7	399.1				
2	42.9	383.0				
4	73.3	259.6				
6	73.4	95.5				
8	72.1	72.5				
10	68.3	63.1	0.120	0.0547	4.94	− 3.10
12	78.0	58.4	0.0707	0.0259	5.98	− 9.72
20	78.0	49.7	0.0371	0.00834	11.46	− 7.75
32	80.5	42.8	0.0285	0.00413	14.37	− 8.61
50	65.0	38.5	0.0228	0.00235	19.72	− 11.62

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

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

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

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

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. The parameter X_{II} is the monomer conversion at which point the monomer

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	0.91	g/ml	
ρ_p	1.05	g/ml	
X_{II}	40.7	%	[20]
$[M]_p$	5.48	mol/l	[20]

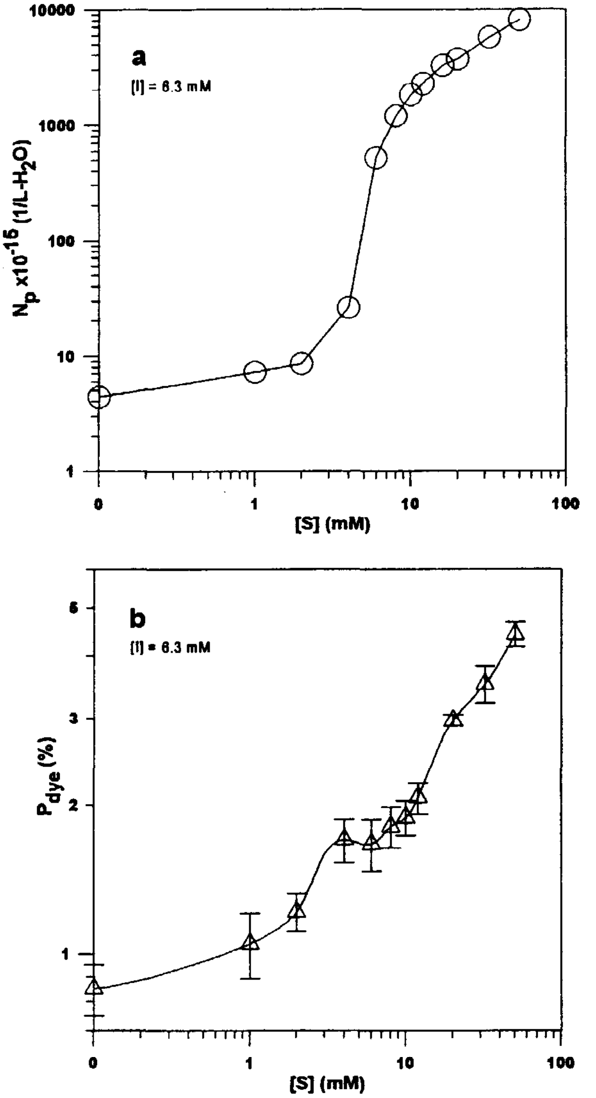

Fig. 2. (a) Final number of latex particles per unit volume of water as a function of the surfactant concentration (slope = 0.89 when [S] > CMC and slope = 0.22 when [S] < CMC) and (b) weight percentage of dye incorporated into the final latex particles as a function of the surfactant concentration (slope = 0.53 when [S] > CMC and slope = 0.12 when [S] < CMC): [I] = 6.3 mM.

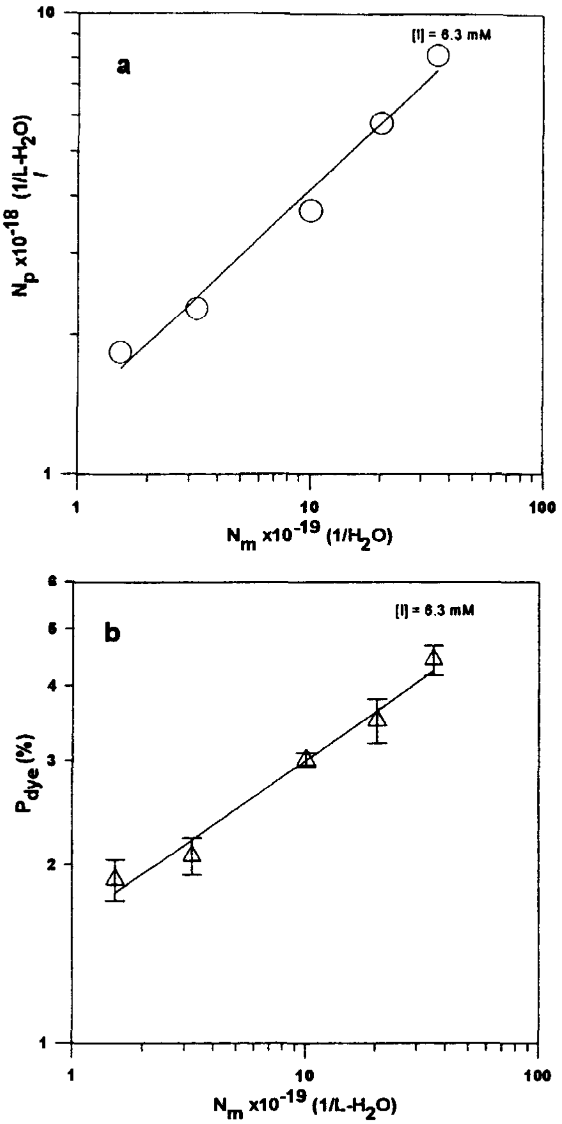

Fig. 3. (a) Final number of latex particles per unit volume of water as a function of the number of micelles per unit volume of water (slope = 0.48) and (b) weight percentage of dye incorporated into the final latex particles as a function of the number of micelles per unit volume of water (slope = 0.27): [I] = 6.3 mM.

droplets disappear (i.e., the end of Smith–Ewart interval II). The parameters 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 particles, respectively, when $X \leq X_{II}$. The kinetic parameters required for computing N_p were determined in this work or obtained from the literature and they are listed in Tables 2 and 3.

Fig. 2*a* shows that N_p is relatively insensitive to changes in [S] when [S] (0.1–2 mM) < CMC (8.2 mM). Thus, the slope obtained from the least-squares best-fitted log N_p versus log[S] straight line is only 0.22. Around the CMC of the aqueous SDS solution, N_p increases sharply when [S] increases from 2 to 10 mM. Above the CMC, N_p is proportional to [S] to the 0.89 power, which is much higher than the theoretical value (0.6) derived for the batch emulsion polymerization. Apparently, the difference in the dependence of N_p on [S] is primarily due to the semibatch process used in this study. Fig. 2*b* shows the corresponding P_{dye} versus [S] data and the sharp transition occurring around the CMC in the log N_p versus log[S] curve has not been observed in this plot. The relationship $P_{dye} \sim [S]^{0.12}$ holds when [S]<CMC. Above the CMC, the slope of the least-squares best-fitted log P_{dye} versus log[S] straight line is 0.53, which is much smaller than that obtained from the log N_p versus log[S] data (0.89).

The number of micelles per unit volume of water (N_m) formed just before the start of polymerization can be

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

	[S] (mM)										
	12	12	12	12	12	12	4	4	4	4	4
[I] (mM)	2.66	5.32	6.30	13.30	21.28	31.92	2.66	5.32	13.30	21.28	31.92
X (%)	76.7	76.0	77.5	79.2	80.5	80.5	51.6	70.4	76.4	80.9	80.5
d_p (nm)	72.1	63.6	58.4	54.2	54.0	60.5	211.3	213.3	142.2	104.9	93.6
R_i/N_m (1/s)	0.011	0.022	0.026	0.055	0.087	0.13					

estimated by the following equation provided that the influence of monomer and dye can be ignored.

$$N_m = ([S] - CMC)/m \quad (3)$$

where m is number of SDS molecules in one micelle (i.e., aggregation number). The values of CMC and m for SDS can be found in Table 3. Fig. 3 also indicates that the slope obtained from the least-squares best-fitted $\log N_p$ versus $\log N_m$ straight line (0.48) is greater than that obtained from the $\log P_{dye}$ versus $\log N_m$ data (0.27) when [S] > CMC. That is, N_p increases more rapidly than P_{dye} does as N_m is increased from 1.53×10^{19} to 3.55×10^{20} 1/L-H_2O. Above the CMC, the difference in the dependence of N_p and P_{dye} on N_m implies that some mechanisms other than micellar nucleation must have been operative in the reaction system. This postulation is further supported by the N_p/N_m and R_i/N_m data listed in Table 2. The ratio N_p/N_m represents the fraction of micelles which can be successfully converted into latex particles if micellar nucleation predominates in the particle formation period. As to the ratio R_i/N_m, it represents the number of free radicals captured per second by one micelle. The term $R_i = 2fk_d[I]$ is the generation rate of free radicals in water, f is the initiation efficiency factor, and k_d is the initiator decomposition rate constant. The kinetic parameters f and k_d required for computing R_i are listed in Table 3. The ratio R_i/N_m decreases significantly with increasing [S]. This trend then leads to the conclusion that the probability of capturing oligomeric radicals by the monomer-swollen micelles to initiate the particle nucleation process decreases with increasing N_m. Thus, the larger the number of micelles present, the smaller is the fraction of micelles which can be successfully transformed into latex particles. This inference is clearly reflected in the N_p/N_m data shown in Table 2, that is, N_p/N_m decreases significantly when [S] increases from 10 to 50 mM (or N_m increases from 1.53×10^{19} to 3.55×10^{20} 1/L-H_2O). However, not all the latex particles are produced by micellar nucleation because an abundant supply of SDS molecules present in the unnucleated micelles is available for stabilizing the primary particles generated in the aqueous phase via homogeneous nucleation. The particle nuclei just formed in the aqueous phase and the growing latex particles may compete effectively with micelles for oligomeric radicals and SDS molecules. Such a competitive process may result in a reduction in the importance of micelles in the particle nucleation period. The number 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. As a consequence, the rate of increase in P_{dye} is slower than the

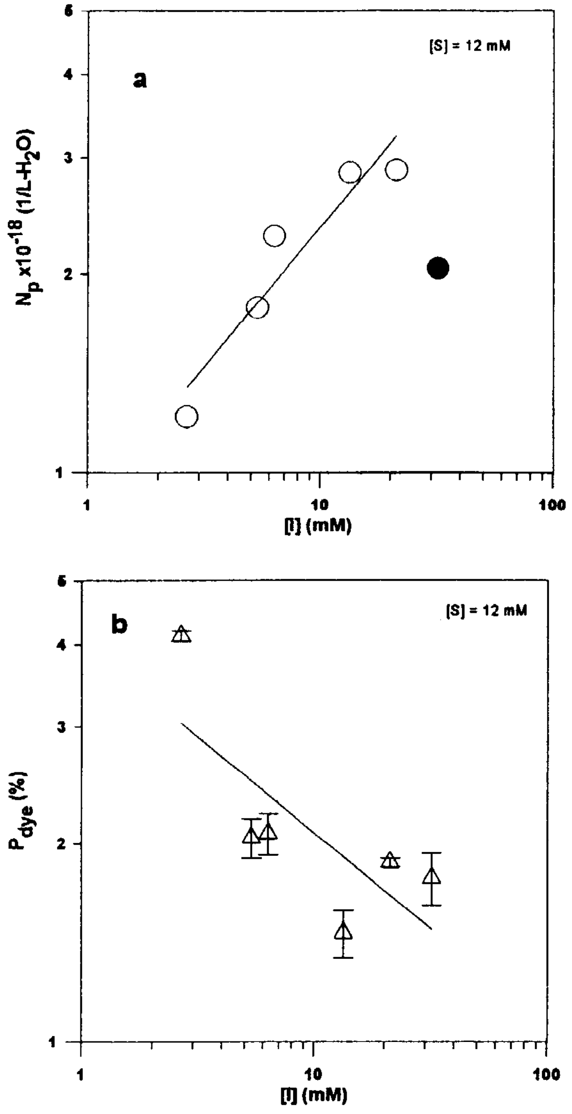

Fig. 4. (a) Final number of latex particles per unit volume of water as a function of the initiator concentration (slope = 0.42) and (b) weight percentage of dye incorporated into the final latex particles as a function of the initiator concentration (slope = − 0.29): [S] = 12 mM.

rate of increase in N_p with [S]. In other words, the slope obtained from the least-squares best-fitted $\log P_{dye}$ versus $\log N_m$ straight line (0.27) is smaller than that obtained from the $\log N_p$ versus $\log N_m$ data (0.48), as shown in Fig. 3.

The parameter $P_{dye,m}$ is defined as the percentage of the added dye initially solubilized in the micelles and it can be estimated by using the solubilization data for the benzene/SDS/H_2O system [15]. The values of $N_{p,m} = N_m(P_{dye} - P_{dye,0})/P_{dye,m}$ and $N_{p,h} = N_p - N_{p,m}$ then represent the number of latex particles originating from micellar nucleation and homogeneous nucleation, respectively, and the calculated results are compiled in Table 2. The parameter $P_{dye,0}$ is the average of the P_{dye} data for the polymerizations with [S] = 0.1–2 mM (i.e., in the absence of micelles). Note that the value of $P_{dye,0}$ is 1.04% (see the P_{dye} versus [S] data in Fig. 2*a*) and it is simply used as the blank in the above mass balance equations. As shown in Table 2, this approach results in a false result that $N_{p,m}$ is larger than N_p and, as a result, $N_{p,h}$ exhibits a negative value. The failure of this mass balance may be due to the limited flocculation among the latex particles during the reaction, as evidenced by the amount of coagulum collected at the end of polymerization (average scrap = 0.6% for this series of experiments). Significant aggregation may lead to a reduction in N_p and, thereby, cause the collapse of the mass balance. The influence of the solubilization of dye and ST in the micelles and the presence of monomer droplets on the values of CMC and *m* may be another factor worthy of further investigation.

As mentioned above, both N_p and P_{dye} are relatively insensitive to changes in [S] when [S] < CMC (see the $\log N_p$ and $\log P_{dye}$ data for the runs with [S] = 0.1–2 mM in Fig. 2). The average of the P_{dye} data is 1.04% and the dye incorporated into the latex particles cannot be attributed to formation of particle nuclei in the continuous phase because the extremely hydrophobic dye is incapable of diffusing from the monomer droplets to the aqueous phase. It is then speculated that nucleation in a small fraction of the dye containing monomer droplets (*ca.* 1%) 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 the transport of dye/ST from the monomer droplets to latex particles. Nevertheless, formation of particle nuclei in water should predominate in the particle nucleation period when [S] < CMC. This is because the number of monomer droplets initially present in the reaction system (10^{13}–10^{14} 1/L-H_2O) is much smaller than that of latex particles produced (10^{15}–10^{16} 1/L-H_2O).

3.2. *Effect of initiator concentration*

In this series of experiments, [S] was kept constant at 12 or 4 mM, whereas [I] was varied from 2.66 to 31.92 mM. The average of the total scrap data is slightly higher (0.8%) for this series of polymerizations. 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 runs with [S] (12 mM) > CMC. Without taking into account the closed circular data point shown in Fig. 4*a*, the slope obtained from the least-squares best-fitted $\log N_p$ versus log[I] straight line is 0.42 Such a dependence of N_p on [I] is consistent with the Smith–Ewart relationship $N_p \sim [I]^{0.4}$ developed for batch emulsion polymerization, but this observation is probably coincidental. Interesting enough, P_{dye} decreases as [I] is increased from 2.66 to 31.92 mM, even though the experimental data are quite scattered (see Fig. 4*b*). The slope obtained from the least-squares best-fitted $\log P_{dye}$ versus log[I] straight line is − 0.29. It is expected that P_{dye} will increase with increasing [I]. The reason for this prediction is that the production rate of free radicals in the aqueous phase ($R_i = 2fk_d[I]$) increases with increasing [I]. At constant [S], the increased R_i may enhance the probability of capturing oligomeric radicals by micelles, as shown by the R_i/N_m data in Table 4. This may thus cause an increase in P_{dye}. 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. The experimental data of $\log N_p$ and $\log P_{dye}$ as a function of log[I] for the runs with [S] = 20 mM also show a similar trend, but the $\log P_{dye}$ versus log[I] data are even more scattered (data not shown here).

It is postulated that nucleation of particle nuclei by homogeneous nucleation becomes more important when [I] increases. The higher the initiator concentration, the larger is the number of latex particles originating from homogeneous nucleation. In addition, the monomer droplets are not the particle nucleation loci due to the keen competition provided by the very large number of micelles and particle nuclei generated in the aqueous phase. Formation of latex particles via homogeneous nucleation does not contribute to incorporation of dye into the latex particles since diffusion of the extremely hydrophobic dye molecules from the 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].

The *X* and d_p data for the polymerizations with [S] (4 mM) < CMC are listed in Table 4. The data of $\log N_p$ and $\log P_{dye}$ as a function of [I] are shown in Fig. 5. In the absence of micelles N_p is strongly dependent on [I], as shown by the slope (1.15) obtained from the least-squares best-fitted $\log N_p$ versus log[I] straight line in Fig. 5*a*. There is no doubt that homogeneous nucleation plays an important role in the polymerization system without micelles. Nucleation taking place in the dye containing monomer droplets, however, cannot be ignored. This is because P_{dye} also increases from 2.2% to 4.0% when [I] increases from 2.66 to 31.92 mM and the relationship $P_{dye} \sim [I]^{0.24}$ holds in this case (see Fig. 5*b*). 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 may increase the probability of capturing oligomeric

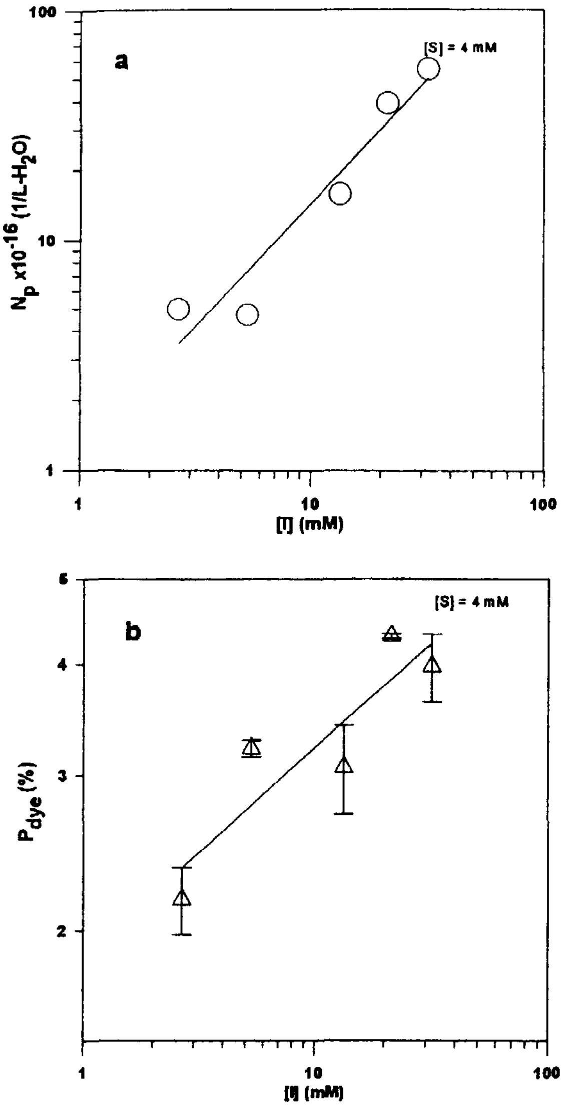

Fig. 5. (a) Final number of latex particles per unit volume of water as a function of the initiator concentration (slope = 1.15) and (b) weight percentage of dye incorporated into the final latex particles as a function of the initiator concentration (slope = 0.24): [S] = 4 mM.

radicals by the monomer droplets and, thereby, lead to an increase in P_{dye} with [I]. Furthermore, the counterion (Na$^+$) concentration in water will also increase with increasing [I]. The enhanced 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 also promote transport of the dye molecules from the monomer droplets to the latex particles and, thereby, result in an increase in P_{dye} with [I].

4. Conclusions

This work has demonstrated the use of a water-insoluble dye to investigate the particle nucleation mechanism involved in the semibatch emulsion polymerization of styrene (ST). Determination of the number of latex particles per unit volume of water (N_p) alone is not sufficient to conclude which particle nucleation mechanism is operative in the course of polymerization. Judging from the data of N_p and weight percentage of dye ultimately incorporated into the latex particles (P_{dye}), the mixed modes of particle nucleation (micellar and homogeneous nucleation) are proposed when the surfactant concentration ([S]) is above its critical micelle concentration (CMC). The attempt to quantitatively determine the fraction of latex particles originating from each nucleation mechanism has not been successful, probably due to such factors as limited flocculation among the latex particles and uncertainty in the values of CMC and aggregation number of surfactant molecules in one monomer-swollen micelle (*m*). In the absence of micelles (i.e., [S] < CMC) most of the latex particles are produced via homogeneous nucleation. However, the monomer droplet nucleation mechanism cannot be ruled out because an appreciable amount of dye can be detected in the resultant latex particles (P_{dye}~1%).

For the polymerizations with [S] > CMC, N_p is proportional to the initiator concentration ([I]) to the 0.42 power, whereas P_{dye} is proportional to [I] to the − 0.29 power. It is postulated that the number of latex particles generated by homogeneous nucleation increases significantly with increasing [I]. This trend then leads to a decrease in P_{dye} when [I] increases. This is because the extremely hydrophobic dye molecules are incapable of diffusing from the monomer droplets to the latex particles born in the aqueous phase. In the absence of micelles both N_p and P_{dye} increase with increasing [I]. The relationships $N_p \sim [I]^{1.15}$ and $P_{dye} \sim [I]^{0.24}$ can be established. Formation of particle nuclei in the aqueous phase (homogeneous nucleation) plays an important role in the polymerization system without micelles. Nucleation taking place in the dye containing monomer droplets, however, cannot be ruled out.

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References

[1] Harkins WD. J Am Chem Soc 1947;69:1428.
[2] Smith WV, Ewart RW. J Chem Phys 1948;16:592.
[3] Smith WV. J Am Chem Soc 1948;70:3695; 1949;71:4077.
[4] Roe CP. Ind Eng Chem 1968;60:20.
[5] Priest WJ. J Phys Chem 1952;56:1077.
[6] Fitch RM, Tsai CH. In: RM Fitch, editor Polymer colloids New York: Plenum, 1971.
[7] Fitch RM. Br Polym J 1973;5:467.
[8] Lichti G, Gilbert RG, Napper DH. J Polym Sci Polym Chem Ed 1983;21:269.

[9] Feeney PJ, Napper DH, Gilbert RG. Macromolecules 1984;17:2520.
[10] Feeney PJ, Napper DH, Gilbert RG. J Colloid Interface Sci 1985;107:159.
[11] Ugelstad J, El-Aasser MS, Vanderhoff JW. J Polym Sci, Polym Lett Ed 1973;11:503.
[12] Ugelstad J, Hansen FK, Lange S. Makromol Chem 1974;175:507.
[13] Chern CS, Chen TJ, Liou YC. Polymer (in press).
[14] Chern CS, Liou YC, Chen TJ. Macromol Chem Phys (in press).
[15] Nagarajan R, Chaiko MA, Ruckenstein E. J Phys Chem 1984;88:2916.
[16] Rehfeld SJ. J Phys Chem 1967;71:738.
[17] Tartar H.V. J Phys Chem 1955;59:1195.
[18] Venable RL, Nauman RV. J Phys Chem 1964;68:3498.
[19] Kolthoff I.. Miller IK. J Am Chem Soc 1951;73:3055.
[20] Harada M, Nomura M, Kojima H, Eguchi W, Nagata S. J Appl Polym Sci 1972;16:811.