

Elucidation of the Miniemulsion Stabilization Mechanism and Polymerization Kinetics

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Received 19 December 2002; accepted 29 January 2003

ABSTRACT: Styrene/hexadecane miniemulsions were polymerized at 50°C using a redox initiator. The miniemulsions and their corresponding latexes were characterized in terms of size, polymerization rate, and surface properties. The resulting data were analyzed to elucidate the miniemulsion stabilization and polymerization mechanisms. It was found that the free surfactant concentration exceeded the critical micelle concentration when large amounts of surfactant (60 mM sodium lauryl sulfate) were used, resulting in simultaneous micellar and droplet nucleation. Most surfactant was on the surface of the droplets (85%) or particles (95%). The fractional surface coverage was proportional to the surfactant concentration to the 0.55 power. Using a particle diameter equation, the number of particles was calculated to be proportional to the surfactant concentration to

the 1.35 power. Through direct particle size measurements, a power of 1.38 was confirmed. The rate of polymerization was determined by reaction calorimetry to be proportional to the number of particles to the 0.59 power, in contrast to classical Smith–Ewart kinetics for conventional emulsions (1.0 power). The average number of radicals per particle was estimated from the rate and number data, and varied with the particle diameter to the 0.97 power. The observed kinetic dependencies were validated through an extension of Smith–Ewart theory. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3987–3993, 2003

Key words: miniemulsions; particle nucleation; polymerization kinetics; polystyrene; latexes

INTRODUCTION

Miniemulsions are submicron dispersions of monomer in water. Miniemulsion droplets are usually formed by the high-shear homogenization of a crude emulsion. Surfactant is used in sufficient quantity to provide the droplets with colloidal stability against coalescence. A hydrophobic costabilizer (often hexadecane) retards the degradation by Ostwald ripening of the miniemulsion droplets. Oligoradicals enter directly into the miniemulsion droplets to initiate polymerization. Aqueous phase nucleation is avoided as a result of the low free surfactant concentration. Although predominant droplet nucleation was observed in submicron emulsions and documented in 1973,¹ the term “miniemulsion” did not appear in the literature until 1980.²

Smith–Ewart³ theory for conventional emulsion polymerizations states that the number of polymer particles (N_p) and the rate of polymerization (R_p) vary with $[SLS]^{0.6}$. It is not likely that miniemulsions follow

the same trends as conventional emulsions, given that the nucleation mechanisms and surfactant distributions differ substantially between the two cases.

In a conventional emulsion, the majority of surfactant is in the water phase as micelles and free surfactant, and particles are nucleated primarily in the monomer-swollen micelles. The monomer droplets are large ($>1 \mu\text{m}$) and have relatively little interfacial area to adsorb surfactant. The droplets supply growing polymer particles with monomer until they are exhausted.

By contrast, in miniemulsions, the monomer droplets are small and the interfacial area is large, so that most of the surfactant resides on the droplet surface, and relatively little is present in the aqueous phase. This reduces the probability of homogeneous nucleation and eliminates micellar nucleation altogether because the free surfactant concentration is below the critical micelle concentration (cmc). Nucleation occurs primarily within the monomer droplets.

The particle size is an important parameter in emulsion polymerization, and control of the particle size is critical in industrial applications. It is possible to manipulate the particle size through the amount of surfactant and the level of shear used in preparing a miniemulsion. To understand the relationships among the particle size, the polymerization rate, and the surface properties, the surfactant concentration in a series

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Contract grant sponsor: National Science Foundation; contract grant numbers: CTS-9628783 and CTS-9980208.

Contract grant sponsor: Emulsion Polymers Liaison Program.

of miniemulsions was varied, the miniemulsions and corresponding latexes were characterized, and the resulting data were analyzed to elucidate the stabilization and polymerization mechanisms.

EXPERIMENTAL

Miniemulsions were prepared with hexadecane (4 wt % based on monomer) as costabilizer and increasing surfactant concentrations (10, 20, 40, 60, and 80 mM SLS based on water). Sodium lauryl sulfate (SLS) was from Fisher Scientific (Pittsburgh, PA) and hexadecane (HD) was from Aldrich (Milwaukee, WI). An inhibitor removal column (Aldrich) was used to clean the styrene monomer (Sigma-Aldrich, St. Louis, MO). Miniemulsions having monomer contents of 20 wt % were prepared using deionized water.

To form the miniemulsions, crude emulsions were first sonified (Branson, Ultrasonics Corp., Danbury, CT; model 450) for 60 s at a power level of 7 with a 60% duty cycle, and then Microfluidized (Microfluidics Corp., Newton, MA; model 110T) for 10 passes. The droplet degradation period between microfluidization and initiation was minimized to 5 min. The miniemulsions were polymerized in an automated reaction calorimeter (Mettler-Toledo, Columbus, OH; RC1 equipped with a 1 L MP10 reactor) to measure the polymerization rates. Polymerizations were carried out at 50°C using a redox-initiator system consisting of ascorbic acid (0.26 wt % based on monomer) and hydrogen peroxide (0.46 wt % based on monomer). A redox-initiator system was chosen for its ability to rapidly generate free radicals for droplet nucleation. The stirrer speed was 300 rpm.

The miniemulsion droplets⁴ and corresponding latexes⁵ were characterized by surfactant titration. The initial and final free surfactant concentrations ($[SLS]_{aq}$) were estimated using surface tensiometry (Sensadyne, Instrument Division, Mesa, AZ; model 6000) and a calibration curve. The fraction of surfactant on the droplet or particle surface (τ) was calculated by mass balance by first subtracting $[SLS]_{aq}$ from the total amount of SLS in the miniemulsion ($[SLS]_{tot}$), and then dividing by $[SLS]_{tot}$. The fractional surface coverage values (θ) and the volume-surface average diameters (D_{vs}) were determined from the titration data and the known values of the surface area coverage per molecule of surfactant (a_s) of 44.0 Å²/molecule on polystyrene⁶ and 71.2 Å²/molecule on styrene/hexadecane.⁴ Particle diameters were confirmed by dynamic light scattering (NICOMP 370, Particle Sizing Systems, Inc., Santa Barbara, CA).

RESULTS AND DISCUSSION

In the series of miniemulsions prepared with increasing $[SLS]_{tot}$, $[SLS]_{aq}$ was measured for each miniemul-

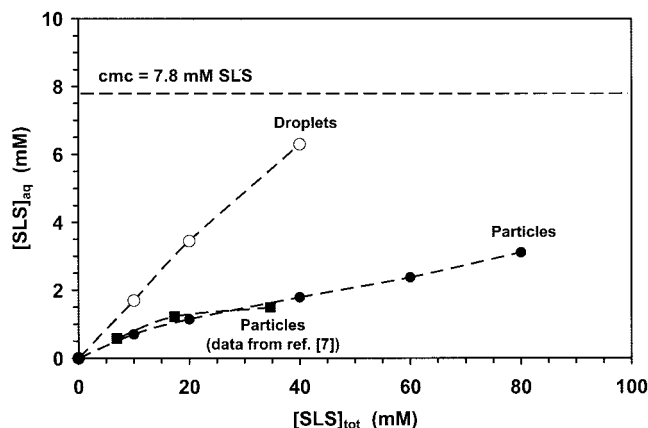


Figure 1 Surfactant concentration in the aqueous phase ($[SLS]_{aq}$) as a function of the total surfactant concentration ($[SLS]_{tot}$) for styrene miniemulsion droplets and polystyrene latex particles (20% monomer); 4 wt % hexadecane based on monomer.

sion and its corresponding latex. The resulting surfactant concentration data are shown graphically in Figure 1. It was found that $[SLS]_{aq}$ increased as $[SLS]_{tot}$ increased. As increasing levels of surfactant were added, the surfactant molecules partitioned between the aqueous phase and the surface of the miniemulsion droplets. At 60 mM $[SLS]_{tot}$, $[SLS]_{aq}$ exceeded the cmc. Secondary (micellar) nucleation occurred simultaneously with droplet nucleation in the miniemulsions with free surfactant concentrations above the cmc.

The free surfactant concentrations in all of the final latexes were below the cmc. $[SLS]_{aq}$ was lower (at the same $[SLS]_{tot}$) in the latex than in the miniemulsion because of the greater energy of adsorption of SLS onto polystyrene than onto styrene. In other words, the latex particles had a greater capacity to adsorb surfactant than the emulsion droplets because of a smaller area per surfactant molecule (44 versus 71.2 Å²/molecule), despite the reduced surface area of the latex particles compared to that of the droplets (Table I).

Experimental $[SLS]_{tot}$ and $[SLS]_{aq}$ data from the literature for a comparable miniemulsion latex system⁷ are also shown in Figure 1 for comparison with the present results. The data were in agreement within the range of surfactant concentrations studied.

Figure 2 illustrates that the fraction of the surfactant residing on the surface of the miniemulsion droplets (τ) is not a strong function of the surfactant concentration, and has an average value of 0.85. This is in agreement with the value of 0.8 (80% of SLS molecules at the droplet interface) given in the literature.⁸

For the latex particles, τ was essentially constant at 0.95. The packing density of SLS was higher (and consequently, τ was greater) on the polystyrene latex particles than on the styrene monomer droplets as a result of a higher energy of adsorption.

TABLE I
Miniemulsion and Latex Properties Resulting from Redox-Initiated Polymerizations at 50°C

	[SLS] _{tot} ^a (mM)				
	10	20	40	60	80
Miniemulsion A_s (cm ²)	2.53×10^7	3.32×10^7	4.57×10^7	—	—
Latex A_s (cm ²)	1.62×10^7	2.34×10^7	3.24×10^7	3.81×10^7	4.49×10^7
Miniemulsion D_{vs} (nm)	81.5	61.7	44.4	—	—
Latex D_{vs} (nm)	107.1	74.3	53.3	45.2	38.4
Latex D_v (NICOMP) (nm)	105.4	75.9	54.6	46.7	39.5

^a The costabilizer concentration was held constant at 4 wt % hexadecane based on monomer.

It has been reported that the fractional surface coverage (θ) in a miniemulsion decreases as the surfactant concentration decreases.⁹ The Freundlich isotherm is a semiempirical equation that can be used to describe the adsorption behavior of dilute surfactants in liquid solutions.¹⁰ The form of the isotherm is $\theta = k[\text{surfactant}]^n$, where k and n are constants. Because the measured droplet and particle θ values were nearly identical at a given surfactant concentration, both sets of data were fit to the same Freundlich isotherm, as shown in Figure 3:

$$\theta = 0.05[\text{SLS}]_{\text{tot}}^{0.55} \quad (1)$$

For latex particles produced by the conventional emulsion polymerization of styrene, it has been noted that $\theta \propto [\text{SLS}]_{\text{tot}}^{0.58}$.¹¹ The exponent is comparable to that determined in eq. (1) for particles produced by miniemulsion polymerization. It is not yet clear why the surface coverage dependencies in emulsion and miniemulsion polymerization might be similar, despite significantly different nucleation mechanisms. Limited aggregation may be one possible explanation.

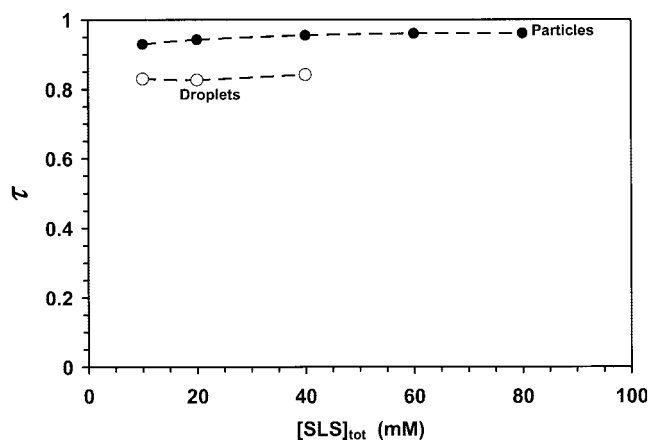


Figure 2 Fraction of the surfactant residing on the particle or droplet surface (τ) as a function of the total surfactant concentration ($[\text{SLS}]_{\text{tot}}$) for styrene miniemulsion droplets and polystyrene latex particles (20% monomer); 4 wt % hexadecane based on monomer.

The radius (R , nm) of the droplets in a miniemulsion can be expressed as a function of the fractional surface coverage (θ) of surfactant [eq. (17) in Paunov et al.¹²]:

$$R = 3\Gamma_{\infty}\theta \frac{V_0}{N_s} \quad (2)$$

where Γ_{∞} is the surfactant surface density at saturation (molecules/nm²), V_0/N_s is the volume of monomer divided by the total number of molecules of surfactant on the surface (cm³ monomer/molecule), and

$$\frac{V_0}{N_s} = \frac{10^{21}M_s}{S\rho_0N_A} \quad (3)$$

where M_s is the molecular weight of the surfactant (g/mol), ρ_0 is the monomer density (g/cm³), N_A is Avogadro's number, and S is the surfactant mass (g) divided by the monomer mass (g).

It can be shown that, for polymer particles, eqs. (2) and (3) are equivalent to

$$D_{vs} = \frac{6 \times 10^{29} \left(\frac{F}{1-F} \right) \left(\frac{\rho_w}{\rho_p} \right) \theta}{\tau[\text{SLS}]_{\text{tot}} N_A a_s} \quad (4)$$

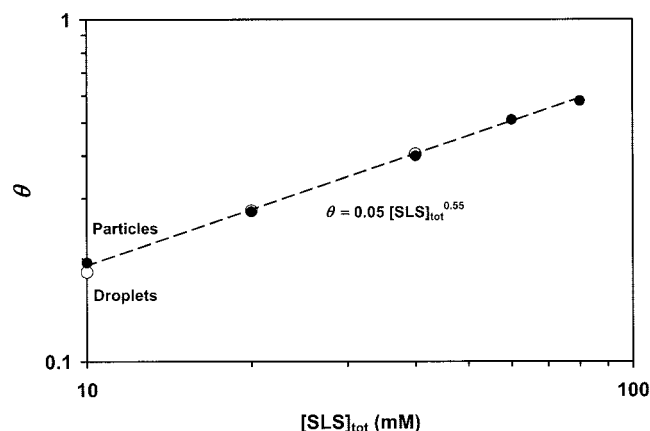


Figure 3 Fractional surface coverage (θ) as a function of total surfactant concentration ($[\text{SLS}]_{\text{tot}}$) for styrene miniemulsion droplets and polystyrene latex particles (20% monomer); 4 wt % hexadecane based on monomer.

where D_{vs} is the volume surface-average particle diameter (nm), F is the polymer mass fraction in the latex, ρ_p is the polymer density (g/cm^3), ρ_w is the water density (g/cm^3), $[\text{SLS}]_{\text{tot}}$ is in mM, and a_s is the area covered per surfactant molecule at surface saturation ($\text{\AA}^2/\text{molecule}$), which equals $100\Gamma_{\infty}^{-1}$ in Paunov's equation.

The diameters of the miniemulsion droplets and the latex particles were measured by surfactant titration, and the particle diameters were verified by dynamic light scattering (NICOMP), as shown in Table I. The trend in particle size is consistent with the established values for comparable miniemulsion latexes, where higher surfactant concentrations produced smaller particle diameters.^{7,9} However, the absolute particle diameters were substantially smaller at a given surfactant concentration in the present case (using microfluidization and redox initiator, and minimizing the droplet degradation period) than were reported in the literature.

Using the measured diameters, the numbers of particles per liter of water (N_p , particles/ $\text{dm}^3 \text{H}_2\text{O}$) were calculated from

$$N_p = \frac{6 \times 10^{24} m x}{\pi \rho_p D_v^3} \quad (5)$$

where m is the total polymer mass (g) divided by the water mass (g), x is the fractional conversion, and ρ_p is in g/cm^3 . Assuming D_v (nm) equals D_{vs} for particles with a fairly narrow size distribution, and substituting eqs. (1) and (4) into eq. (5):

$$N_p = 10^{-63} \left(\frac{m x \rho_p^2}{36 \pi} \right) \left(\frac{\tau N_A a_s (1 - F)}{0.054 \rho_w F} \right)^3 [\text{SLS}]_{\text{tot}}^{1.35} \quad (6)$$

Equation (6) holds for miniemulsion droplets as well as for latex particles. The initial number of droplets

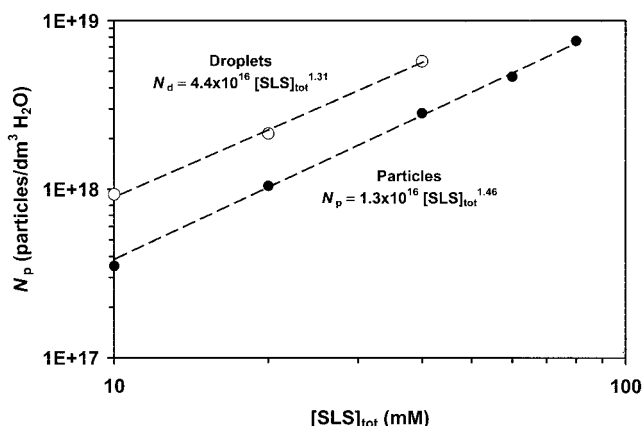


Figure 4 Number of particles (N_p) as a function of total surfactant concentration ($[\text{SLS}]_{\text{tot}}$) for styrene miniemulsion droplets and polystyrene latex particles (20% monomer); 4 wt % hexadecane based on monomer.

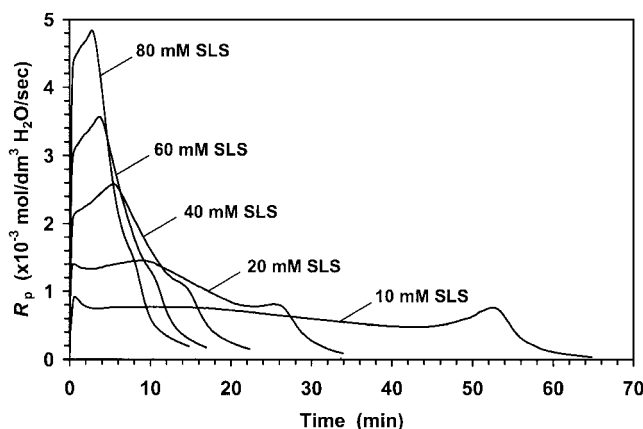


Figure 5 Rate of polymerization (R_p) as a function of time for styrene miniemulsions (20% monomer); 4 wt % hexadecane based on monomer; redox-initiated; $T_r = 50^\circ\text{C}$.

differed from the final number of particles, possibly as the result of a slight deviation in the values of a_s for this particular system from the literature values. Such a discrepancy would affect the absolute diameter, but would not affect the slope of the $\log D_{vs}$ versus $\log [\text{SLS}]_{\text{tot}}$ line. The numbers of particles and droplets were calculated from the size data, and are shown on a log–log scale in Figure 4. By averaging the exponents for the droplets (1.31) and the particles (1.46), it was determined that

$$N_p \propto [\text{SLS}]_{\text{tot}}^{1.38 \pm 0.07} \quad (7)$$

The number of particles is a stronger function of $[\text{SLS}]_{\text{tot}}$ than expected by Smith–Ewart theory ($N_p \propto [\text{SLS}]_{\text{tot}}^{0.6}$). The exponent in eq. (7) is in agreement with the one determined in eq. (6). Both exponents were derived from independently measured data sets. Thus, θ and D_{vs} are rigorously linked through eq. (4). In other words, the dependency of N_p on $[\text{SLS}]_{\text{tot}}$ is a direct consequence of the θ dependency on $[\text{SLS}]_{\text{tot}}$.

N_p data for comparable miniemulsion latexes were obtained from two different sources in the literature.^{7,9} Through logarithmic analysis, it was determined that the dependencies of N_p on $[\text{SLS}]_{\text{tot}}$ differed substantially, with one being just under unity (0.92),⁹ whereas the other exceeded a value of 2 (2.19).⁷ The variation in the exponents from the value given in eq. (7) is probably the result of differences in the monomer/hexadecane contents, miniemulsification methods, aging times, initiator types, and polymerization temperatures.

The rates of polymerization [R_p , $\text{mol}/(\text{dm}^3 \text{H}_2\text{O} \text{s}^{-1})$] for the series of miniemulsions with increasing surfactant concentration were measured by reaction calorimetry, and are shown as a function of polymerization time in Figure 5. As the surfactant concentration was increased, R_p (max) also increased, as ex-

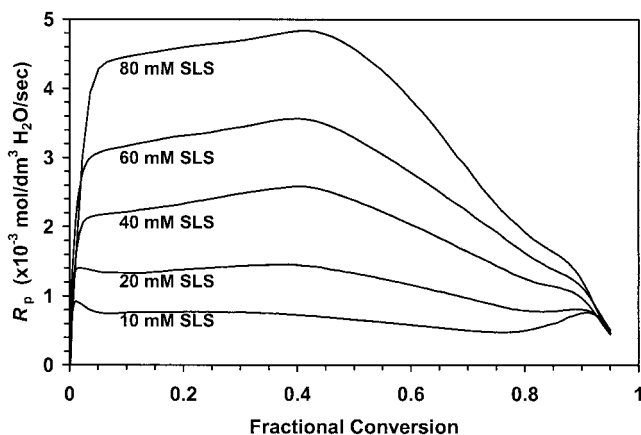


Figure 6 Rate of polymerization (R_p) as a function of fractional conversion for styrene miniemulsions (20% monomer); 4 wt % hexadecane based on monomer; redox-initiated; $T_r = 50^\circ\text{C}$.

pected from the corresponding increase in N_p . The shapes of the kinetic profiles reveal additional information about the miniemulsion polymerization mechanism. The kinetic profiles are qualitatively similar to those reported for conventional emulsion polymerizations of styrene¹³ (except for a smaller gel effect), even though the nucleation mechanisms are completely different. The similarity in the shapes of the kinetic profiles may be related to the slight water solubility of styrene, and the resulting redistribution of monomer from large (offsize) droplets acting as reservoirs during polymerization. The kinetic profiles shown in Figure 5 are consistent in shape with those of other researchers.^{14,15}

The rates of polymerization are shown as a function of fractional conversion (x) in Figure 6. The maximum rate of polymerization occurred at about 40% conversion in each case (not counting the spike in R_p at low conversion in the polymerization employing 10 mM SLS).

The polymerization rate maxima [R_p (max)] are shown in Figure 7 as a function of the number of particles (N_p). Through logarithmic analysis, it was determined that

$$R_p(\text{max}) \propto N_p^{0.59} \quad (8)$$

The exponent 0.59 differs significantly from classical Smith–Ewart kinetics in which R_p varies with $N_p^{1.0}$.

R_p and N_p values were estimated from comparable miniemulsion polymerizations in the literature,¹⁵ and these data were also analyzed logarithmically, yielding a dependency of $R_p \propto N_p^{0.55}$, which is in reasonable agreement with the present findings [eq. (8)].

The polymerization rate can be expressed as

$$R_p = \frac{k_p[M]_p N_p \bar{n}}{N_A} \quad (9)$$

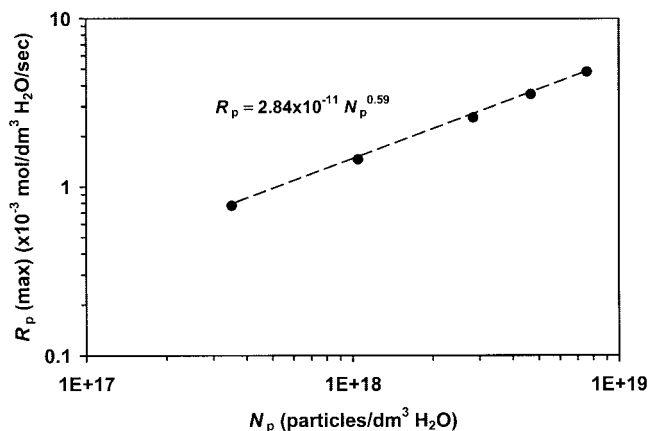


Figure 7 Maximum rate of polymerization [R_p (max)] as a function of number of particles (N_p) for styrene miniemulsions (20% monomer); 4 wt % hexadecane based on monomer.

where k_p is the propagation rate constant [$\text{L}/(\text{mol s}^{-1})$], $[M]_p$ is the monomer concentration in the polymer particles (mol/L), and \bar{n} is the average number of radicals per particle. For each miniemulsion, \bar{n} [at R_p (max)] was calculated from eq. (9) using the experimental R_p (max) and N_p data shown in Figure 7. k_p at 50°C was calculated from a correlation given by Buback and Kuchta.¹⁶ Using the monomer molecular weight (104 g/mol) and the monomer and polymer densities (0.909 and 1.05 g/cm³, respectively), $[M]_p$ was estimated from the fractional conversion measurements at R_p (max) shown in Figure 6. \bar{n} [at R_p (max)] values are shown as a function of particle diameter in Figure 8. From these data, it was determined that

$$\bar{n} [\text{at } R_p(\text{max})] \propto D_{vs}^{0.97} \quad (10)$$

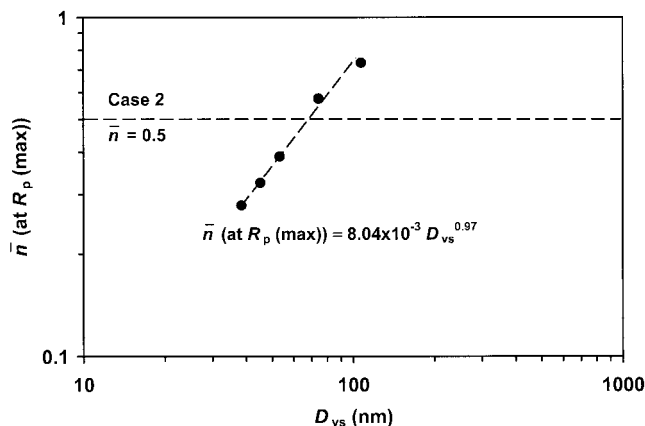


Figure 8 \bar{n} [at R_p (max)] as a function of final particle diameter (D_{vs}) for styrene miniemulsions (20% monomer); 4 wt % hexadecane based on monomer; redox-initiated; $T_r = 50^\circ\text{C}$.

where \bar{n} is directly proportional to the particle diameter, and no discontinuity is seen for Smith–Ewart case 2 kinetics ($\bar{n} = \frac{1}{2}$). Instead, the kinetics passed from case 1 ($\bar{n} < \frac{1}{2}$) to case 3 ($\bar{n} > 1$) without disruption or transition. Previous investigators also found that \bar{n} was a linear function of particle diameter in the miniemulsion homopolymerization of methyl methacrylate, and suggested that this dependency may be the result of a high radical desorption rate.¹⁷

A theoretical equation relating R_p and N_p in miniemulsions is derived here using the principles of Smith and Ewart.³ According to Smith–Ewart theory, radical desorption becomes increasingly more important when particle diameters decrease. Assuming that radicals are likely to exit the small miniemulsion particles, the fraction of the particles that contain a radical at any given time will be small (Smith–Ewart case 1), and the total number of particles containing a radical [approximated from the recursion eq. (1) in Smith and Ewart] is:

$$N_1 \cong \frac{\rho'v}{k_0a} \quad (11)$$

where N_1 is the number of reaction loci containing one radical, ρ' is the overall radical entry rate, v is the volume of a single particle, k_0 is the exit rate coefficient, and a is the interfacial area of a single particle.

Smith and Ewart assumed that the rate of diffusion of a radical from the water phase into a polymer particle is equal to the rate of radical entry per particle (ρ'/N_p):

$$\frac{\rho'}{N_p} = 2\pi\mathbf{D}D_p c_w \quad (12)$$

where \mathbf{D} is the diffusion coefficient of the radicals in the water phase, D_p is the particle diameter, and c_w is the concentration of the radicals in the water phase.

In the small miniemulsion particles, termination is likely to take place instantaneously when a second radical enters a polymerizing particle, in which case the rate of radical termination (dn/dt , where n is the number of free radicals) is given by eq. (7) of Smith and Ewart:

$$\frac{dn}{dt} = -2\left(\frac{\rho'}{N_p}\right)N_1 \quad (13)$$

Substituting eqs. (11) and (12) into eq. (13) and assuming that the rate of radical termination is equal and opposite in sign to the rate of radical generation (ρ)

$$\rho = 2(2\pi\mathbf{D}D_p c_w)\left(\frac{\rho'v}{k_0a}\right) \quad (14)$$

Assuming that every radical generated eventually enters the polymer particles ($\rho = \rho'$) and solving for c_w

$$c_w = \frac{k_0a}{4\pi\mathbf{D}D_p v} \quad (15)$$

In eq. (4) of their study, Smith and Ewart use a partition coefficient (α) to relate the radical concentration in the water phase to the radical concentration in the particles (c_p) under conditions when radical entry and exit are rapid:

$$\alpha = \frac{c_p}{c_w} \quad (16)$$

Substituting eq. (15) into eq. (16) and solving for c_p gives

$$c_p = \frac{\alpha k_0 a}{4\pi\mathbf{D}D_p v} \quad (17)$$

Given that $a = \pi D_p^2$ and $v = (\pi/6)D_p^3$

$$c_p = \frac{3\alpha k_0}{2\pi\mathbf{D}D_p^2} \quad (18)$$

Solving eq. (5) for D_v yields

$$D_v = \left(\frac{6mx}{\pi\rho_p N_p}\right)^{1/3} \quad (19)$$

Assuming that D_p refers to the volume-average particle diameter (D_v) and substituting eq. (19) into eq. (18) gives

$$c_p = \left(\frac{3\alpha k_0}{2\pi\mathbf{D}}\right)\left(\frac{\pi\rho_p N_p}{6mx}\right)^{2/3} \quad (20)$$

The rate of polymerization has been expressed by Smith and Ewart, in their eq. (2a), as

$$R_p = k_p[M]_p V_p c_p \quad (21)$$

where V_p is the total volume of the swollen polymer particles in the system.

Because $V_p = N_p v = mx/\rho_p$, substituting eq. (20) into eq. (21) results in

$$R_p = k_p[M]_p \left(\frac{\alpha k_0}{\mathbf{D}}\right)\left(\frac{3mx}{32\pi\rho_p}\right)^{1/3} N_p^{2/3} \quad (22)$$

It was found experimentally in Figure 7 that for miniemulsions, $R_p \propto N_p^{0.59}$, which is within experimental error of the dependency of R_p on N_p derived in eq. (22).

It is apparent from eqs. (9) and (22) that

$$\bar{n} = \left(\frac{N_A \alpha k_0}{D} \right) \left(\frac{3mx}{32\pi\rho_p} \right)^{1/3} N_p^{-1/3} \quad (23)$$

Upon substitution of eq. (5) into eq. (23)

$$\bar{n} = \left(\frac{N_A \alpha k_0}{64D} \right) D_v^1 \quad (24)$$

The linear relationship between \bar{n} and D_v as given by eq. (24) has been verified experimentally in Figure 8 (where D_v and D_{vs} are used interchangeably, given that the particle size distribution produced by the polymerization of styrene/hexadecane miniemulsions can be quite narrow¹⁸).

CONCLUSIONS

In the styrene miniemulsions prepared with 10, 20, 40, 60, and 80 mM SLS/4 wt % hexadecane and polymerized at 50°C using a redox initiator system, the surface coverage, particle size, and reaction kinetics were measured. The free surfactant concentration in the miniemulsions was typically low, but exceeded the cmc when large amounts of surfactant were used ($[SLS]_{\text{tot}} \geq 60 \text{ mM}$). As a result, micellar nucleation occurred simultaneously with droplet nucleation in the miniemulsions prepared with high surfactant concentrations. All of the miniemulsion latexes prepared in this study had free surfactant concentrations below the cmc. The surfactant adsorbed more strongly to the polymer particles (i.e., a_s was smaller) because of a higher energy of adsorption. Most of the surfactant was on the surface of the droplets (85%) or particles (95%), regardless of the surfactant concentration.

It was found experimentally that $\theta \propto [SLS]_{\text{tot}}^{0.55}$. From the surface coverage dependency and the particle diameter equation, the relationship between the number of particles and $[SLS]_{\text{tot}}$ was calculated to be $N_p \propto [SLS]_{\text{tot}}^{1.35}$. This finding was confirmed by direct measurement resulting in $N_p \propto [SLS]_{\text{tot}}^{1.38}$. Analyses of two sets of literature data yielded exponents of 0.92 and 2.19, demonstrating that the particle numbers were

highly dependent on recipe, emulsification, and reaction conditions.

The rate of polymerization was measured using calorimetry, and followed $R_p(\text{max}) \propto N_p^{0.59}$, in contrast to classical Smith–Ewart kinetics for conventional emulsions. The average number of radicals per particle was calculated for the redox-initiated polymerizations from the rate and number data, and varied as $\bar{n} \propto D_{vs}^{0.97}$. The kinetics of miniemulsion polymerization were derived through an extension of Smith–Ewart theory.

The authors acknowledge with great appreciation the partial funding from the National Science Foundation (Grants CTS-9628783 and CTS-9980208) and the additional financial support from the Emulsion Polymers Liaison Program.

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