Macromolecules **2000,** *33,* 4347−4353

Effect of a Mixed Anionic−Nonionic System of Surfactants on the Entry and Exit of Free Radicals into Polystyrene Particles

Damien Colombié, E. David Sudol, and Mohamed S. El-Aasser*

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Iacocca Hall, 111 Research Drive, Bethlehem, Pennsylvania 18015

Received December 8, 1999; Revised Manuscript Received March 28, 2000

ABSTRACT: Seeded emulsion polymerizations of styrene were conducted with various ratios of the anionic surfactant sodium lauryl sulfate and the nonionic surfactant Triton X-405 adsorbed on the polystyrene latex particles. The polymerization kinetics were monitored utilizing the Mettler RC1 reaction calorimeter and subsequently analyzed to determine the effects of the adsorbed surfactants on the entry of free radicals into the particles and the desorption of radicals from the particles. All the reactions were run in interval III at 50 °C, and "zero−one" conditions were determined to exist in order to analyze the data by the "slope−intercept" method. Using the RC1, the start of the polymerization could be determined within 4 s. No significant effect of the surfactant ratio (40% surface coverage) was noted on the pseudo-first-order entry rate coefficients within experimental error. Larger experimental errors were noted in the determination of the pseudo-first-order exit coefficients with no discernible effect of the surfactant ratio being observable.

Introduction

Mixtures of anionic and nonionic surfactants have been commonly used for the synthesis and stabilization of polymer latexes. Anionic surfactants provide electrostatic stability as described by the DLVO theory.[1,2] Electrostatic repulsion is created between particles by electrical double layers, which are created primarily from the presence of the anionic chain end of the surfactants (e.g., sulfate or sulfonate groups). This repulsion is a kinetic effect dependent on many parameters such as ionic strength and pH. This dependency can be a major drawback in terms of stability of the latex. Nonionic or polymeric surfactants provide steric stabilization. The repulsion between particles is provided by the thermodynamically favored steric repulsion of the adsorbed materials.[3,4] It is therefore practical to use mixtures of anionic and nonionic surfactants in emulsion polymerization to combine the different stabilization mechanisms. Most industrial emulsion polymerization processes use mixtures of anionic and nonionic emulsifiers. A very common process can be described as follows: the reaction is started with the anionic surfactant, and the nonionic is added at a higher conversion or as a poststabilizer. When combinations of anionic and nonionic surfactants are used in emulsion polymerization, a layer of both emulsifiers is adsorbed on the surface of the particles. This layer of surfactants can be beneficial to the stability of the system. Nevertheless, it may affect the kinetics of the reaction as the oligomeric free radicals formed in the aqueous phase have to diffuse through this interfacial film to enter the particles. In addition, exiting free radicals (monomeric radicals) must diffuse through this layer to escape the particles.

The measurement of the absolute values of the entry and exit rate coefficient has been the subject of numerous investigations. Gilbert[5] and co-workers have widely studied the kinetics of particle growth. A simple experimental technique to evaluate the pseudo-first-order entry (ρ) and exit (k) rate coefficients was developed using seeded emulsion polymerization. The technique, referred to as the "slope−intercept" approach, consists of monitoring very carefully the conversion as a function of time in the early moments of a seeded emulsion polymerization (which can be initiated chemically or by using γ-radiolysis). The method was applied under various conditions. Adams et al.[6] studied the effect of the extent of surface coverage by an anionic surfactant on polystyrene particles on the entry and exit of the free radicals. They also studied the effect of ionic strength. From their experiments, no effect of the surfactant coverage or the ionic strength on the entry or exit of radicals to and from the polystyrene particles was noted within experimental error. In the case of electrostatic stabilization, the surfactant displacement from the particle surface to allow adsorption was not found to be the rate-determining step for entry of the oligomeric radicals. However, when a steric stabilizer was used, the results were different. Kusters et al.[7] studied the influence of an "Inisurf" (surface active initiator with a poly(ethylene oxide) tail) on the kinetics of particle growth in the presence of a poly(ethylene oxide) nonylphenol as nonionic stabilizer. The seed was prepared using an anionic surfactant (which was subsequently removed) and a small amount of potassium styrenesulfonate, before a known amount of the nonionic surfactant was added. By γ-radiolysis relaxation studies, the exit coefficient was determined to be an order of magnitude lower in the case of the nonionic surfactant as compared to an anionic emulsifier. This was explained by a slow diffusion of the exiting radical through the hairy layer of a particle coated with the polymeric surfactant. Coen et al.[8] also studied the effect of poly(acrylic acid) on the entry and exit in emulsion polymerization. A seed in which a small amount of PAA was embedded (creating a 5 nm deep layer at the particle surface) was synthesized. Then, the "slope−intercept" procedure was used, and the electrosteric stabilizer was found to greatly decrease both ρ and k. This decrease was again attributed to the presence of a "hairy layer" around the particles. The study of the influence of a

10.1021/ma9920590 CCC: $19.00

Table 1. Recipe for the Interval III Seeded Emulsion Polymerization of Styrene Using a 92 nm Monodisperse Polystyrene Seed at 50 °C (Experiments DCI3-1 to DCI3-8)

ingredient	amount	concentration
monodisperse polystyrene seed latex (cleaned, 5% solids, $D_n = 92$ nm)	600.00 g	1.2×10^{17} particles/dm^3
styrene	38 g	0.4 mol
sodium lauryl sulfate	see Table 2	
Triton X-405	see Table 2	
potassium persulfate	0.16 g[a]	1.0 mM[a]
sodium bicarbonate	0.09 g	1.8 mM

[a] Experiment DCI3-3 was run with 0.0160 g of KPS (i.e., 0.1 mM).

Table 2. Surfactant Amounts (in grams) Used in the Interval III Seeded Emulsion Polymerizations of Styrene Using a 92 nm Monodisperse Polystyrene Seed at 50 °C (Experiments DCI3-1 to DCI3-8)

experiment	SLS	Triton X-405	SLS/Triton X-405 molar ratio
DCI3-1[a]	0.80		
DCI3-2[a]	0.80		
DCI3-3[a]	0.80		
DCI3-4	1.24		
DCI3-5	0.49	1.09	3.1
DCI3-6	0.22	1.50	1.0
DCI3-7	0.08	1.70	0.3
DCI3-8		1.81	

[a] The latex seed was not cleaned for experiments DCI3-1 to DCI3-3 (trial runs).

mixed layer of surfactants has not yet been reported.

The method developed by Gilbert et al. is experimentally simple. However, it also has some drawbacks. The values of ρ and k are determined with a large error (±50% at best). Asua et al. recently showed that systematic errors in the procedure could lead to dramatic errors in the evaluation of the results.[9] For example, if an error of 30 s in the detection of the start of the reaction is made, it will result in a 200% error in the determination of k. Another drawback of the "slope−intercept" method is that ρ represents a global entry rate for the system. It is therefore dependent on the initiator concentration and the number of particles. The calculations by the "slope−intercept" method also include an adjustable parameter α (referred to as the "fate parameter"), which accounts for the reentry of desorbed radicals into the particles.[10] Asua et al.[9] proposed and evaluated a method for determining k_a (an intrinsic parameter representing the adsorption rate coefficient) and k using a minimum of 9−12 different experiments, run with various initiator concentrations and numbers of particles. This method would, however, require an extensive number of experiments with the various ratios of the two surfactants and, thus, was not adopted here.

In the present study, reaction calorimetry was first evaluated as a possible technique to obtain the data necessary to use the "slope−intercept" approach in the determination of the pseudo-first-order entry and exit rate coefficients. One advantage of using the Mettler RC1 is based on the extensive data available, every 2 s of a reaction. The pseudo-first-order entry and exit rate coefficients were then estimated for different surfactant compositions, using sodium lauryl sulfate as an anionic surfactant and Triton X-405 (octylphenoxypolyethoxyethanol with 40 average number of ethylene oxide units; from Union Carbide) as nonionic surfactant.

Experimental Section

Materials. The seeded experiments were performed using the ingredients given in Table 1, with the variation in the amounts of added surfactants being reported in Table 2. The styrene monomer (Aldrich) was washed three times with a 10 wt % NaOH solution to remove the inhibitor, rinsed three times with deionized water, and distilled no more than 2 weeks prior to a polymerization. The monodisperse polystyrene latex used (LS-1039E, Dow Chemical Co.) had a number-average diameter of 92 nm (determined by electron microscopy[11]). The surface charge of the particles was found (by ion exchange/conductometric titration) to be 2.5 μC/cm^2, which is in the range expected for such a seed prepared with an anionic surfactant and persulfate initiator. In reactions DCI3-4 to DCI3-8, the latex (5.0% solids) was cleaned for 3 weeks by serum replacement to remove the surfactant and impurities in the latex particles prior to use. Deionized water was used for all the reactions. Ultrapure Bioreagent sodium lauryl sulfate (J. T. Baker) was used as the anionic emulsifier. Triton X-405 (70% solution in water, Aldrich) was dried in an oven for 24 h at 70 °C and used as the nonionic emulsifier. Potassium persulfate (Aldrich) was recrystallized from deionized water before it was used as the initiator. Sodium bicarbonate (J. T. Baker) was used as received.

Polymerizations. The polymerizations were run in the Mettler RC1 reaction calorimeter. The rate of polymerization (R_p) can be calculated from the heat of reaction (Q_r), according to the following equation:

$$R_p = \frac{Q_r}{V_{aq}\Delta H_p} \tag{1}$$

where V_{aq} is the volume of the aqueous phase and ΔH_p is the molar heat of polymerization. The fractional conversion (x) at time t is calculated according to the following equation:

$$x(t) = \frac{\int_0^t Q_r(t)\,dt}{\int_0^{t_f} Q_r(t)\,dt}\, x_{grav}(t_f) \tag{2}$$

where $Q_r(t)$ is the heat of polymerization at time t, t_f is the time at which the reaction is stopped, and $x_{grav}(t_f)$ is an independent measurement of the fractional conversion at the end of the reaction (performed by gravimetry).

The general procedure for running the experiments is as follows. The seed latex was filtered and poured into a glass bottle. The surfactant(s) and buffer were added, and the mixture was stirred at 300 rpm for 2 h using a magnetic bar. The monomer was then added and allowed to swell the latex particles overnight. The mixture was added to the Mettler RC1 reaction calorimeter, and nitrogen was passed through the reactor headspace for 60 min. The nitrogen flow rate was kept constant in all experiments so that the removal of oxygen was very similar in all cases. The purging time was kept constant. The reactor temperature was subsequently ramped to 50 °C in 15 min, and the agitation rate was set to 400 rpm. The initiator was dissolved in 5.0 g of deionized water and heated to the reaction temperature to minimize the heat perturbation upon addition. A short induction period (5−6 min) was obtained after the addition of initiator to allow an accurate detection (within 4 s) of the start of reaction. At the end of the reaction, 2 mL of a 1 wt % aqueous solution of hydroquinone was added to the latex to inhibit the formation of radicals.

Characterization. All final latexes were examined by TEM to check for the presence of secondary nucleation. For these samples, the remaining monomer was removed by vacuum distillation. In some cases, the samples were negatively stained using uranyl acetate. A Phillips 400 transmission electron microscope was used with a magnification of 28 000×.

Results and Discussion

The "Slope−Intercept" Technique in the Mettler RC1 Calorimeter. a. Theory. As mentioned in the Introduction, the "slope−intercept" method is a technique suitable for the determination of the pseudo-first-order entry and exit rate coefficients. This method was devised and used extensively at the University of Sydney by the group of Gilbert and Napper[5−8] and is briefly reviewed here. It is based on a careful monitoring of the fractional conversion versus time curve at the beginning of a seeded emulsion polymerization. The following assumptions are made. If the seed latex particles are small enough ($D_n < 100$ nm) and if the initiator level is kept low, the entry of a free radical into a particle containing a growing radical essentially results in termination ("zero−one" approximation, i.e., there is either 0 or 1 free radical in any given polymer particle). In the following derivation, the reentry of the desorbed radicals is neglected even though an extension of the model can take this into account. If N_0 and N_1 are the numbers of particles containing zero and one free radicals, respectively, then the average number of free radicals per particle ($\bar{n}$) is given by

$$\bar{n} = \frac{N_1}{N_0 + N_1} \tag{3}$$

The time evolution of N_0 and N_1 is given by the following system of coupled differential equations:

$$\frac{\mathrm{d}N_0}{\mathrm{d}t} = -\rho N_0 + (\rho + k)N_1$$
$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = \rho N_0 - (\rho + k)N_1 \tag{4}$$

If the number of particles is normalized ($N_0 + N_1 = 1$), the solution for this system is given by eq 5.

$$N_1 = \bar{n} = \frac{\rho}{2\rho + k} + \left(\bar{n}_0 - \frac{\rho}{2\rho + k}\right) \exp[-(2\rho + k)t] \tag{5}$$

where $\bar{n}_0$ is the initial average number of free radicals per particle. The rate equation can be written as

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = \frac{k_p N_p [\mathrm{M}]_p}{n_M^0 N_A} \bar{n} = A\bar{n} \tag{6}$$

where x is the fractional conversion, k_p is the propagation rate constant (dm^3/(mol s)), N_p is the number of particles per dm^3 of aqueous phase, $[\mathrm{M}]_p$ is the monomer concentration in the particles (mol/dm^3), n_M^0 is the initial number of moles of monomer per dm^3 of water, and N_A is Avogadro's number. In a seeded experiment starting in the presence of monomer droplets (interval II), A is constant and the early moments of the reaction can be modeled by integration of the rate equation using eq 5. The result is given by eq 7.

$$x(t) = \frac{A}{2\rho + k}\left(\rho t + \left(\bar{n}_0 - \frac{\rho}{2\rho + k}\right)(1 - \exp[-(2\rho + k)t])\right) \tag{7}$$

In a real seeded experiment starting in interval II, the conversion−time curve becomes linear a few minutes after the beginning of the reaction. (The exponential factor in eq 7 is negligible for long times.) From the experimental determination of the slope and intercept of the linear part of the conversion−time curve, it is possible to calculate the entry and exit rate coefficients.

If the experiment is started when all the monomer is located in the particles (interval III), the monomer concentration in the particles is given by

$$[\mathrm{M}]_p = [\mathrm{M}]_{p0}[1 - x(t)] \tag{8}$$

The integration of the rate equation results in the following expression.

$$-\ln[1 - x(t)] = \frac{A_0}{2\rho + k}\left(\rho t + \left(\bar{n}_0 - \frac{\rho}{2\rho + k}\right)(1 - \exp[-(2\rho + k)t])\right) \tag{9}$$

The "slope−intercept" analysis can be performed by plotting $-\ln(1 - x)$ as a function of time. When reentry of the free radicals is taken into account, the preceding calculations can be extended. For styrene/polystyrene systems, a fate parameter of 1 is usually used as the desorbed free radicals undergo complete reentry into the particles.[10]

The "slope−intercept" technique must be used under very strict conditions. First, the seed particles must be monodisperse and should have a small diameter. Second, the initiator concentration should be low enough to result in an average number of free radicals per particle at steady state lower than 0.5. Third, the beginning of the reaction must be determined with great precision (within 10−20 s) to limit the error on the determination of the rate coefficients. In this regard, the use of reaction calorimetry was considered to be advantageous: data can be collected every 2 s, allowing detection of the start of reaction with good accuracy. The RC1 reaction calorimeter also provides a direct determination of the rate of polymerization, making it possible to determine at which point the rate becomes constant (pseudo-steady-state). The main drawback of the RC1 reactor is the relatively high volume of seed latex required for an experiment (approximately 0.6 dm^3), especially if this seed latex has to be cleaned prior to being used.

b. Experiments Starting in Interval III. In this series of experiments (DCI3-1 to DCI3-8), the monomer-to-polymer mass ratio was 1.2. As described in the experimental procedure, the monomer was allowed to fully swell the polymer particles, and no monomer phase was visible before the start of polymerization even when the stirring was turned off.

In Figure 1, the rate of polymerization and the fractional conversion of the seeded emulsion polymerization of styrene starting in Interval III are plotted as a function of time (experiment DCI3-1). The rate curve rises to a maximum in about 13 min at which point the rate of polymerization decreases until the onset of the gel effect (around 60 min after the beginning of the reaction). No constant rate period is noted in this experiment as no extra source of monomer is available to feed the particle growth.

Experiment DCI3-1 was run a second time in order to check the reproducibility of the RC1 technique (experiment DCI3-2). The results are depicted in Figure 2. An excellent reproducibility was obtained especially in the first 25 min of reaction in which the "slope−intercept" analysis is performed. The corresponding curves for the average number of free radicals per

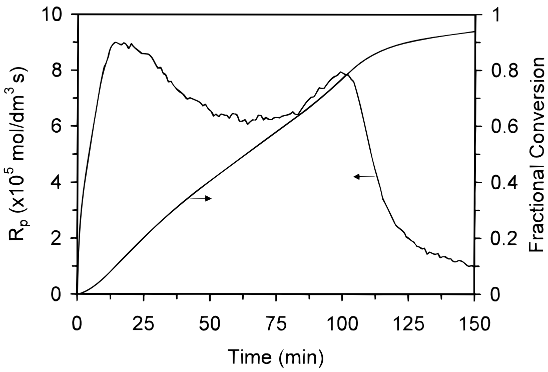

Figure 1. Rate of polymerization and fractional conversion as a function of time in the seeded emulsion polymerization of styrene using a 92 nm polystyrene seed latex and SLS as surfactant at 50 °C (monomer-to-polymer mass ratio 1.2; [KPS] = 1.0 mM; experiment DCI3-1).

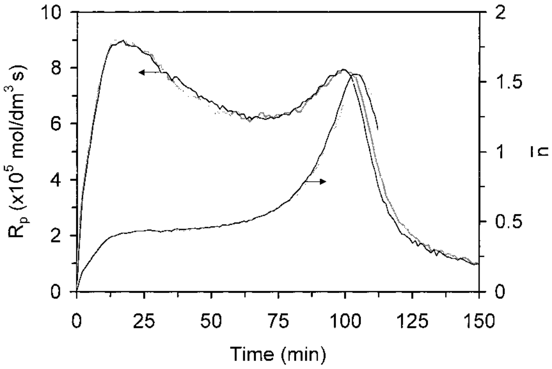

Figure 2. Rate of polymerization and average number of free radicals per particle as a function of time in two seeded emulsion polymerizations of styrene using a 92 nm polystyrene seed latex and SLS as surfactant at 50 °C (monomer-to-polymer mass ratio 1.2; [KPS] = 1.0 mM; experiments DCI3-1 and DCI3-2).

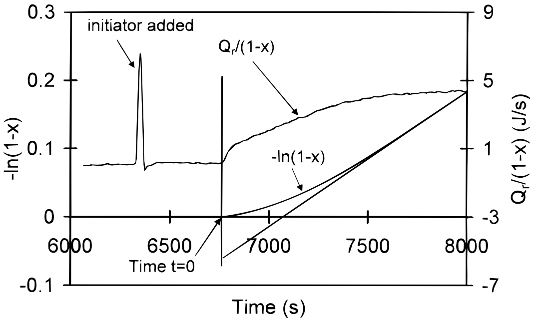

Figure 3. Illustration of the use of reaction calorimetry for the determination of kinetic parameters via the "slope−intercept" method in the seeded emulsion polymerization of styrene using a 92 nm polystyrene seed latex and SLS as surfactant at 50 °C (monomer-to-polymer mass ratio 1.2; [KPS] = 1.0 mM; experiment DCI3-1).

Table 3. Determination of the Kinetic Parameters in the Seeded Emulsion Polymerization of Styrene Using a 92 nm Polystyrene Seed Latex at 50 °C Starting in Interval III (Experiments DCI3-1 to DCI3-3)

experiment	[KPS] (mM)	$\bar{n}_{s-s}$	ρ ($\times10^3$ s^{-1})	k ($\times10^3$ s^{-1})
DCI3-1	1.0	0.42	1.3	0.11
DCI3-2	1.0	0.42	1.3	0.11
DCI3-3	0.1	0.22	0.23	0.15

particle are also plotted on this graph. The average number of free radicals per particles can be obtained from the rate of polymerization, according to eq 10:

$$\bar{n} = \frac{N_A R_p}{k_p[M]_p N_p} \tag{10}$$

where N_A is Avogadro's number, R_p is the rate of polymerization determined with the RC1 reaction calorimeter (mol/(dm^3 s)), k_p is the propagation rate coefficient (240 dm^3/(mol s), Friis and Hameliec[12]), $[M]_p$ is the monomer concentration in the particles (mol/dm^3), and N_p is the number of particles per dm^3 of aqueous phase. Since these experiments were conducted in interval III, the monomer concentration in the particles was always below saturation (5.5 M)[13] and decreased from the beginning of the reaction. All the styrene is assumed to be located in the polystyrene particles, and the monomer concentration in the particles can be calculated according to the following equation:

$$[M]_p = \frac{\dfrac{1-x}{M_0}}{\dfrac{1-x}{\rho_m} + \dfrac{x}{\rho_p}} \tag{11}$$

where x is the fractional conversion, M_0 is the molar mass of styrene (104.75 g/mol), ρ_m is the density of styrene (905 g/dm^3), and ρ_p is the density of polystyrene (1050 g/dm^3).

As shown in Figure 2, $\bar{n}$ increases for 13 min to reach a constant value around 0.4 (within the range of "zero−one" conditions). The "slope−intercept" analysis performed on the data obtained from the RC1 reactor is detailed in Figure 3. The heat of polymerization given by the RC1 calorimeter is normalized (Q_r/(1 − x), where Q_r is the heat of reaction). At about 6300 s, there was an "exotherm" due to the addition of the warmed initiator solution (1.0 mM). This addition was followed by an induction period in which the remaining oxygen was consumed by the initiator. At 6720 s (±2 s), the reaction starts, and the resulting conversion−time curve was calculated by the RC1 evaluation software and an independent measurement of the final conversion (eq 2).

The normalized constant rate period starts around 7700 s. In interval III, the slope and intercept of the −ln(1 − x) versus time curve are used for the determination of ρ and k. The results are given in Table 3. As shown in this table, the reproducibility of the RC1 technique in interval III is good. The sensitivity of the technique was tested by lowering the initiator concentration by 1 order of magnitude, keeping all other parameters constant. The rate of polymerization and the average number of free radicals per particle as a function of fractional conversion for experiment DCI3-3 (0.1 mM KPS) are depicted in Figure 4. Both curves are noisier than in the previous experiments, due to the low heats of polymerization involved. However, it is possible to use the data for the determination of the kinetic coefficients. The results are given in Table 3. The entry rate decreased from 1.3 to 0.23 s^{-1}, and the exit rate remained in the same range. As a result, the average number of free radicals per particle decreased from 0.42 to 0.22.

From these data, it is possible to conclude that the RC1 calorimeter can be used as a good tool to collect interval III seeded emulsion polymerization data for the determination of the pseudo-first-order entry and exit

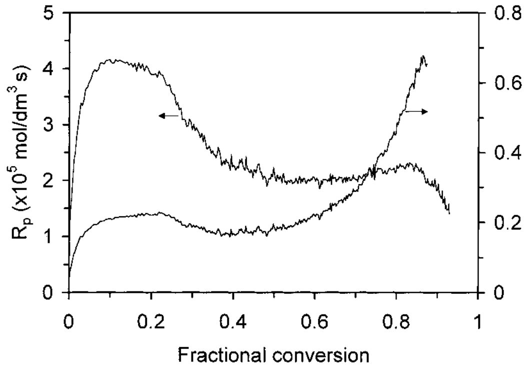

Figure 4. Rate of polymerization and average number of free radicals per particle as a function of fractional conversion in the seeded emulsion polymerization of styrene using a 92 nm polystyrene seed latex and SLS as surfactant at 50 °C (monomer-to-polymer mass ratio 1.2; [KPS] = 0.1 mM; experiment DCI3-3).

rate coefficients (via "slope–intercept" analysis). The advantages of using the RC1 are an accurate detection (within 4 s) of the start of the reaction and the possibility to evaluate the pseudo-steady-state period from the direct measurement of the rate of polymerization. The main sources of errors result from monomer loss during the purging step (evaluated to be around 10% by gas chromatography) and the determination of the final conversion by gravimetry. Other disadvantages are the relatively high volume of latex required for each experiment (0.6 dm^3) and the possible contamination by inhibitors or retarders in the reaction vessel.

Variation of Surface Coverage. a. Kinetic Results. In this section, the surfactant surface coverage is varied, and the pseudo-first-order entry and exit rate coefficients are determined using the preceding technique. Prior to being used, the monodisperse polystyrene seed latex was extensively cleaned by serum replacement to remove the surfactants and other impurities (including inhibitors and retarders).

In this series of experiments, the initial surfactant surface coverage can be estimated. The area occupied by one molecule of emulsifier was assumed to be 44 and 170 Å^2 for SLS[14] and Triton X-405,[15] respectively ($a_{s\,SLS}$ and $a_{s\,Triton\,X-405}$), since the surface of the particles is not saturated with the two surfactants. The diameter of the swollen particles (d_{sw}) can be calculated as follows (assuming additive volumes):

$$d_{sw} = 2\left[\frac{3}{4\pi N_{p\,tot}}\left(\frac{m_p}{\rho_p} + \frac{m_m}{\rho_m}\right)\right]^{1/3} \qquad (12)$$

where $N_{p\,tot}$ is the total number of particles in the system, m_m and m_p are the mass of monomer and polymer, respectively, and ρ_m and ρ_p are the densities of monomer and polymer, respectively. The percent coverage can be calculated according to the following equation:

$$\%\ \text{coverage} = \frac{N_{SLS}a_{sSLS} + N_{Triton\,X-405}a_{s\,Triton\,X-405}}{4\pi N_{p\,tot}\left(\frac{d_{sw}}{2}\right)^2} \qquad (13)$$

where N_{SLS} and $N_{Triton\,X-405}$ are the number of molecules of SLS and Triton X-405, respectively, in the system. The surfactant amounts in the system were controlled and corresponded to approximately 40% surface coverage of the swollen particles using the calculations given above. The molar ratio of SLS to Triton X-405 was varied to check for significant variations in the entry and exit rate coefficients as a function of the nature of the surface coverage.

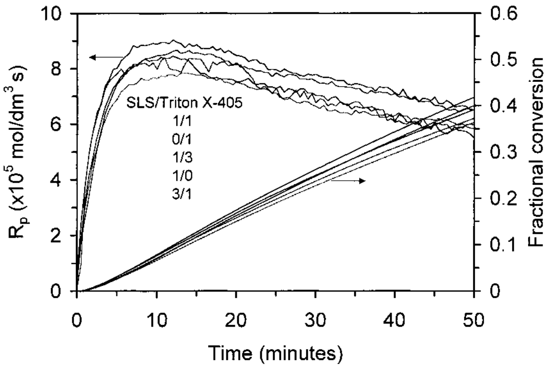

Figure 5. Rate of polymerization and fractional conversion as a function of time in the seeded emulsion polymerizations of styrene using a 92 nm polystyrene seed latex and various molar ratios of SLS and Triton X-405 as emulsifiers at 50 °C (monomer-to-polymer mass ratio 1.2; [KPS] = 1.0 mM; experiments DCI3-4 to DCI3-8).

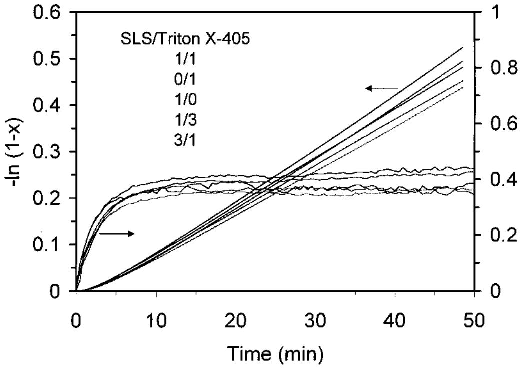

Figure 6. Average number of free radicals per particle and −ln(1 − fractional conversion) as a function of time in the seeded emulsion polymerization of styrene using a 92 nm polystyrene seed latex and various molar ratios of SLS and Triton X-405 as emulsifiers at 50 °C (monomer-to-polymer mass ratio 1.2; [KPS] = 1.0 mM; experiments DCI3-4 to DCI3-8).

Figure 5 shows the rate of polymerization and the fractional conversion as a function of time for the seeded emulsion polymerizations of styrene starting in interval III and using various SLS to Triton X-405 molar ratios (1/0, 3/1, 1/1, 1/3, 0/1). There is little variation in the rate of polymerization and the fractional conversion as a function of surface coverage, especially in the first 20 min of reaction, during which the "slope–intercept" analysis is performed. No clear correlation between the surfactant ratios and the rate maxima is noted. Reactions with a 1/3,1/0, and 3/1 SLS to Triton X-405 molar ratio seem to be slightly slower than the other two. These differences could be attributed to small variations in the initial oxygen level in the system, as oxygen as been suspected to act not only as an inhibitor but also as a retarder.[16] Reactions with a low rate of polymerization could show some sensitivity to these variations.

In Figure 6, the average number of free radicals per particle and $-\ln(1 - x)$ are plotted as a function of time. The pseudo-steady-state is attained within 10–12 min for experiments DCI3-4 to DCI3-8. The slope of the "normalized" fractional conversion will be determined between 12 and 22 min.

Table 4. Determination of the Kinetic Parameters in the Seeded Emulsion Polymerization of Styrene Using a 92 nm Polystyrene Seed Latex at 50 °C Starting in Interval III for Various Ratios of SLS and Triton X-405 (Experiments DCI3-4 to DCI3-8)

experiment	DCI3-4	DCI3-5	DCI3-6	DCI3-7	DCI3-8
$\bar{n}_{s-s}$	0.37	0.35	0.41	0.37	0.39
ρ ($\times 10^3$ s^{-1})	2.6	2.1	2.7	2.8	2.1
k ($\times 10^3$ s^{-1})	0.4	1.1	0.2	1.3	0.4
SLS/Triton X-405 molar ratio	1/0	3/1	1/1	1/3	0/1

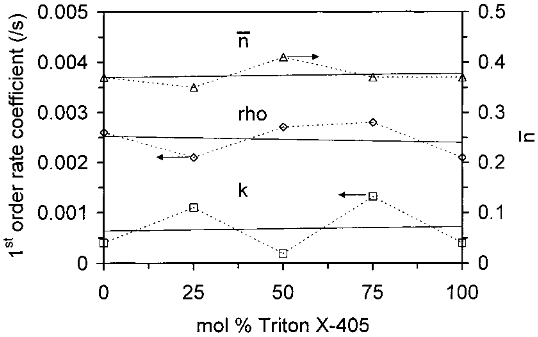

Figure 7. Pseudo-first-order entry (ρ) and exit (k) rate coefficients and average number of free radicals per particle as a function of the molar percentage of Triton X-405 in the seeded emulsion polymerization of styrene using a 92 nm polystyrene seed latex and various amounts of SLS and Triton X-405 as emulsifiers at 50 °C (monomer-to-polymer mass ratio 1.2; experiments DCI3-4 to DCI3-8).

b. "Slope−Intercept" Analysis. The preceding data were analyzed using the method presented above. The results are presented in Table 4 and in Figure 7. The values for the average number of free radicals per particle and the entry rate coefficient do not show any obvious dependence on the surfactant surface composition, within experimental error. Only relatively large changes in these coefficients can be used in any analysis. In this study, the changes in the entry coefficient are within the range of experimental error. These values are within the same order of magnitude as those found by Adams et al.[6] with various degrees of SLS surface coverage on polystyrene particles (1.3×10^{-3} /s). No effect of the extent of SLS surface coverage on radical entry was noted in this study.

The exit coefficient is particularly sensitive to error in these chemically initiated runs. With a large error (70% in Figure 7), no clear trend is noted for the dependence of k on the ratio of the two surfactants at the surface. TEM examination of each latex resulting from experiments DCI3-4 to DCI3-8 was performed. No secondary nucleation was detected as the resulting latexes are essentially monodisperse. Therefore, the "zero−one" approximation was valid as $\bar{n}_{s-s}$ was below 0.5.

Overall, this series of experiments showed that the radical entry and exit rate coefficients are not significantly affected by the various ratios of SLS and Triton X-405 at the surface of the particles. This is in contrast to the case when poly(acrylic acid) was embedded at the surface of a polystyrene seed,[6] where the results obtained from the "slope−intercept" approach indicated a significant decrease in the entry rate (from 3.1×10^{-3}/s to 2.0×10^{-4}/s at pH 7 for a latex of radius 48 nm) when the electrosteric stabilizer was used. In the present study, it is possible that the molecular weight of the Triton X-405 is not large enough to create an actual barrier to entry. As mentioned above, the "slope−intercept" technique has proven to be useful when large variations in the entry and exit rates occur. It is not able to detect small variations in the coefficients. As mentioned in the Introduction, the measurement of entry and exit rate coefficients is a very difficult task, and perhaps in this case alternate methods (i.e., Asua et al.[9]) should be investigated. Furthermore, Triton X-405 is known to be a surfactant with a distribution of EO chain lengths. There may be a preferential adsorption of the shorter EO chain length surfactant molecules on the particle surface that may reduce any barrier to entry. It would be interesting to study the effect of highly fractionated PEO type surfactants on the radical entry and exit rate coefficients.

Summary and Conclusions

In this study, the "slope−intercept" approach[5] was used to determine the effect of various ratios of SLS and Triton X-405 at the surface of the particles on the pseudo-first-order entry and exit rate coefficients of the free radicals. The experimental technique was adopted for use with data obtained from the Mettler RC1 reaction calorimeter. Experiments starting in interval III at low initiator concentrations (1.0 mM) were run. The advantages of using the RC1 are the accurate detection of the start of a reaction (within 4 s) and a direct measurement of the pseudo-steady-state interval. However, some error was introduced by the occurrence of monomer loss during the nitrogen purge and some possible contamination by some inhibitors and retarders. Nonetheless, the reproducibility of the technique was acceptable.

When the molar ratio of SLS to Triton X-405 was varied (keeping a constant surface coverage of approximately 40%), little influence on the polymerization rate versus time curves was noted during the first 25 min of reaction (in which the data treatment is performed). The "slope−intercept" analysis was used to obtain ρ and k, assuming simple zero−one kinetics in which the fate of desorbed free radicals is ignored. The entry rate coefficient was not significantly affected by the variations in emulsifier surface composition, within the sensitivity of the method and the experimental error. The exit rate coefficient also did not show any significant trend with surfactant surface composition. The overall average number of free radicals per particle at steady state was also independent of the surfactant surface composition. All the runs were validated with TEM, and no secondary nucleation was noted. All reactions followed the "zero−one" approximation as $\bar{n}$ remained lower than 0.5 at the pseudo-steady-state.

Acknowledgment. Financial support from Elf Aquitaine and Elf Atochem is greatly appreciated.

References and Notes

(1) Derjaguin, B. V.; Landau, L. *Acta Physicochim. USSR* **1941**, *14*, 633.
(2) Verwey, E. J. W.; Overbeek, J. G. In *Theory of Stabilization of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.
(3) Ottewill, R. H. *J. Colloid Interface Sci.* **1977**, *58*, 357.
(4) Napper, D. H. *Polymeric Stablilization of Colloidal Dispersions*; Academic Press: New York, 1983.
(5) Gilbert, R. G. *Emulsion Polymerization, A Mechanistic Approach*; Academic Press: London, 1995.
(6) Adams, M. E.; Trau, M.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Aust. J. Chem.* **1988**, *41*, 1799.

(7) Kusters, J. M. H.; Napper, D. H.; Gilbert, R. G.; German, A. L.; *Macromolecules* **1992**, *25*, 7043.
(8) Coen, E. M.; Lyons, R. A.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 5128.
(9) Asua, J. M.; Adams, M. E.; Sudol, E. D. *J. Appl. Polym. Sci.* **1990**, *39*, 1183.
(10) Whang, B. C.; Napper, D. H.; Ballard, M. J.; Gilbert, R. G.; Lichti, G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1117.
(11) Miller, C. M. Ph.D. Dissertation, Lehigh University, 1995.
(12) Friis, G. N.; Hameliec, A. E. *J. Polym. Sci., Part A: Polym. Chem.* **1974**, *12*, 251.
(13) Varela de la Rosa, L. Ph.D. Dissertation, Lehigh University, 1996.
(14) Ahmed, S. M.; El-Aasser, M. S.; Pauli, G. H.; Poehlein, G. W.; Vanderhoff, J. W. *J. Colloid Interface Sci.* **1980**, *73*, 388.
(15) Colombié, D.; Landfester, K.; Sudol, E. D.; El-Aasser, M. S. *J. Colloid Interface Sci.* **1998**, *202*, 554.
(16) Lopez de Arbina, L.; Gugliotta, L. M.; Barandiaran, M. J.; Asua, J. M. *Polymer* **1998**, *39*, 4047.

MA9920590