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Effect of a Reactive Surfactant and Its Polymeric Counterpart on the Kinetics of Seeded Emulsion Polymerization of Styrene

Xiaoru Wang, Bito Boya, E. David Sudol, and Mohamed S. El-Aasser*

Emulsion Polymers Institute and Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

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ABSTRACT: Seeded emulsion polymerizations of styrene using the reactive surfactant sodium dodecyl ally sulfosuccinate (TREM LF-40) and its polymeric counterpart, poly(TREM), were carried out, and their reaction kinetics were compared to those obtained using the conventional surfactant sodium lauryl sulfate (SLS). The reaction rate decreased using TREM LF-40 and poly(TREM), compared to SLS. For TREM LF-40, this behavior was attributed to the participation of TREM LF-40 as an allylic monomer in copolymerization and/or chain transfer reactions at the surface of the particles. For poly(TREM), the decrease was considered to be caused by the formation of a “hairy” adsorbed layer of the polymeric surfactant on the particles, which acts as a barrier decreasing the diffusion of the radicals into the particles. It was also found that the rate decreased with increasing TREM LF-40 concentration as expected, this being attributed to increased reaction at the surface of the particles with increasing surface coverage by the surfactant. However, over the range of poly(TREM) concentrations studied, no such trend was apparent, perhaps indicating a saturation of the effect of poly(TREM) on the entry of the radicals. These results were supported by the molecular weights of the resulting polymers. Compared to the latexes polymerized with SLS as the stabilizer, the polystyrene molecular weights of the latexes stabilized with TREM LF-40 were smaller. For poly(TREM), the resulting polystyrene molecular weights were larger than obtained for the SLS stabilized seed, considered to be consequence of a decrease in the entry rate of the radicals into the polymer particles.

Introduction

Reactive surfactants[1−6] have been widely used and studied for their unique advantages in emulsion polymerization, such as the chemical incorporation of the surfactant onto the polymer particles, the increased stability of the final latex, and the elimination of surfactant migration during film formation. Polymeric surfactants,[7] on the other hand, can increase the latex stability against electrolyte acting as steric stabilizers. However, particle nucleation and growth, and the entry and exit of radicals in to and out of the particles, have not been studied extensively using reactive surfactants and their polymeric counterparts. To separate the effects on particle nucleation and growth, seeded emulsion polymerizations are commonly carried out where the conversion vs time behavior can be used to estimate the radical entry and exit rate coefficients under some specific experimental conditions.

Emulsion polymerization kinetics are usually described by[8]

$$M_0 \frac{\mathrm{d}x}{\mathrm{d}t} = R_\mathrm{p} = k_\mathrm{p} \frac{N_\mathrm{p}}{N_\mathrm{A}} \bar{n} M_\mathrm{p} \equiv A\bar{n} \tag{1}$$

where M_0 is the initial monomer concentration in the reaction (mol/dm^3), x is the reaction fractional conversion, t is the reaction time (s), R_p is the reaction rate (mol/(dm^3 s)), k_p is the propagation rate coefficient (dm^3/(mol s)), N_p is the number of particles per unit volume of the aqueous phase (1/dm^3), N_A is Avogadro’s constant (/mol), $\bar{n}$ is the average number of radicals per particle, M_p is the monomer concentration in the latex particles (mol/dm^3), and A is a conversion factor (system specific). When this equation is applied to a seeded emulsion polymerization, especially for a simple zero−one system (in this system, all particles contain either zero or one free radical due to the instantaneous termination in particles containing more than one radical), only entry and exit are rate-determining. At its simplest, this analysis ignores the fate of exited free radicals and the reentry of desorbed free radicals.[8] When the reaction conditions are chosen carefully, the zero−one assumption is suitable for many seeded emulsion polymerization systems. Using conversion−time data, the pseudo-first-order entry (ρ) and exit (k) rate coefficients can be estimated using what has become known as the “slope−intercept” method.[8] For reference, the methodology is reproduced in the Supporting Information.

For conventional surfactants, such as SLS, the extent of the surface coverage on a polystyrene seed and the ionic strength reportedly have no effect on the entry and exit of radicals within experimental error.[9−15] Electrosterically stabilized polystyrene seed latexes, synthesized with a copolymer of styrene and acrylic acid incorporated in a second stage polymerization, were used in seeded polymerizations by Gilbert and co-workers.[11,12] Their results showed that, under specific conditions of pH and surface coverage, entry and exit of the radicals in to and out of the polymer particles were reduced compared to a conventional surfactant. The explanation was that the “hairy” layer on the surface of the polymer particles acts as a barrier to the diffusing radicals. Also, it has been found that the overall rate coefficient for radical entry into particles was independent of the particle size.[8,11−15]

Studies of the effect of a reactive surfactant on the entry and exit rate coefficients have not been performed. It would be of interest to relate the results obtained for the entry and exit rate coefficients in seeded emulsion

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* To whom correspondence should be addressed.

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polymerizations with the kinetics of conventional emulsion polymerizations using the same reactive surfactant. This could hopefully further the fundamental understanding of the process. The reduction of both entry and exit coefficients could occur because of the presence of an electrosteric stabilizer formed by copolymerization or homopolymerization of the reactive surfactant. This material creates a highly viscous region around the polymer particles (called a "hairy layer") and decreases the rate of diffusion of monomeric (exiting) and oligomeric (entering) species through this region.[11,12,16,17] Studies, such as the effect of the polymeric version of a reactive surfactant and its concentration (surface coverage), have not yet been reported.

From studies of the conventional emulsion polymerization of styrene using the reactive surfactant sodium dodecyl allyl sulfosuccinate (TREM LF-40), some questions still remain regarding the kinetics and mechanism.[18] Although the rate of polymerization increased with increasing TREM LF-40, in contrast with those reported previously for vinyl acetate, where the rate *decreased* with increasing TREM LF-40 *and* N_p,[4] the results indicated that there was no one-to-one correspondence between the rate of polymerization and the number of particles (i.e., $R_p \not\propto N_p^{1.0}$) as is normally found for the emulsion polymerization of styrene ($R_p \propto N_p^{1.0}$). The same dependency between R_p and N_p was found to exist at all initiator levels (4−8 mM) over the range of surfactant concentration (20−50 mM) studied ($R_p \propto N_p^{0.7}$). In contrast, at a fixed surfactant concentration and varying initiator concentration, the expected results were obtained ($R_p \propto N_p^{1.0} \propto [I]^{0.4}$). Also, questions remain as to the effect of the reactive surfactant on the average number of radicals per particle ($\bar{n}$) and the entry and exit rate coefficients of the radicals. Seeded emulsion polymerization studies should be helpful in understanding the behavior of this reactive surfactant and should also provide further supporting evidence to explain the unusual kinetics and mechanism of conventional emulsion polymerizations using the reactive surfactant.[18]

Experimental Section

Materials. Styrene (Aldrich) was washed with 10 wt % aqueous NaOH (Fisher Scientific) and DI (deionized) water and distilled under vacuum prior to use. Buffer ($NaHCO_3$, Aldrich) and initiator ($Na_2S_2O_8$, FMC Corp.) were analytical grade. TREM LF-40 was used as received (Henkel Corp.). Deionized water was used in all experiments. Sodium lauryl sulfate (SLS, Fisher Scientific) was used as the conventional surfactant. THF (Aldrich) was used as solvent in GPC measurements. A 92 nm diameter monodisperse polystyrene latex (LS1039E, Dow Chemical Co.) was used in the seeding studies.

Poly(TREM) was prepared by solution polymerization of TREM LF-40 (28.08 g) with $NaHCO_3$ (10 mM) as buffer, $Na_2S_2O_8$ (16 mM) as initiator, and DI water (360 g) as the solvent. The reaction was carried out at 60 °C for 12 h and 90 °C for an additional 9 h to obtain a high conversion and to completely decompose the initiator. The molecular weight of the poly(TREM) was measured by vapor pressure osmometry to be 6000 ± 500 g/mol.[18]

Seeded Emulsion Polymerizations. Prior to the seeding studies, the seed latex was first cleaned of the surfactant and electrolytes remaining from its preparation. The serum replacement method was used for this purpose. This was carried out by passing deionized water through a low solids content latex (5%) confined in a filtration cell. The conductivity of the fluid flowing out of the cell was monitored and compared to the conductivity of the DI water. The cleaning was considered complete when the conductivities were the same.

Table 1. Seeded Emulsion Polymerization Recipe

ingredient	amount
seed latex (10% solids)	40.0 g
styrene	4.5 g
SLS, TREM LF-40, or poly(TREM)	varied
$Na_2S_2O_8$	1−4 mM
$NaHCO_3$	1−4 mM
DI water	14 g

The reaction recipes are given in Table 1. DI water, the seed latex (10 wt % solids), buffer, and the surfactant were mixed and stirred for ~3 h to allow sufficient time for equilibrium adsorption of the surfactant on the polymer particles to be established. All surfactant concentrations were chosen to be well below the saturation values (i.e., no micelles present). After equilibration, the monomer was added, and the mixture was stirred overnight to allow complete swelling of the particles with the monomer. The monomer/polymer weight ratio (1.125/1) was chosen so as to conduct the seeded polymerizations in interval III. Before the reaction, the system was degassed by aspirator vacuum for about 1.5 min at 30 mmHg to prevent bubbles from being formed in the system and to remove some of the dissolved O_2. This provided for a reasonable induction period. The reactions were performed at 50 °C in an all-glass 25 mL dilatometer stirred by a Teflon-coated magnetic bar. Conversion vs time curves were obtained from the change in the capillary height in the dilatometer recorded every 30 s. The final conversion was double checked by gas chromatography (GC, Hewlett-Packard 5890) and gravimetry. Particle size and size distributions of the final latexes were measured by capillary hydrodynamic fractionation (CHDF model 1100, Matec Applied Sciences) and transmission electron microscopy (TEM, Philips EM 400). This was necessary to check for secondary nucleation or aggregation, which would invalidate the use of the kinetics for determining entry and exit rate coefficients by the "slope−intercept" method.[8] Only results are reported here where neither of these were detected.

The reaction conditions were carefully chosen for the system to obey "zero−one" kinetics, such that $\bar{n}$ was always less than 0.5. Estimation of the radical entry and exit rate coefficients in the presence of the reactive surfactant assumes that there is no influence of copolymerization and chain transfer reaction to the surfactant. This may certainly be a bad assumption in the case of TREM LF-40, and therefore "apparent" values of ρ and k are reported. These were estimated assuming that polymerization only involved propagation of styrene monomer in the seed particles (using the k_p of styrene and the monomer concentration in the particles) as carried out for the other systems. The effect of copolymerization and chain transfer to TREM LF-40 at the surface of the particles is not taken into account, and thus the term "apparent" is used.

Molecular Weight Measurements. The latexes were dried at room temperature and then dissolved in THF (1 wt % polymer). The polymer solution was then filtered through a 0.45 μm filter before injection into the gel permeation chromatograph (GPC, Millipore-Waters). The number-average molecular weight ($\bar{M}_n$) was obtained from the molecular weight distribution.

Results and Discussion

Effect of Degassing Time on the Reaction. During the initial part of the study, degassing was found to cause significant monomer loss, which could lead to inaccurate estimations of ρ and k. By measuring the monomer concentration by GC before and after degassing (30 mmHg) for different degassing times, the best degassing time was determined to be 1.5 min. No bubbles were produced in the dilatometer, and the monomer loss was about 6−8%, which is still relatively high. However, to avoid bubble formation, this was the lower limit for the degassing time. The monomer loss was taken into account in the later calculations.

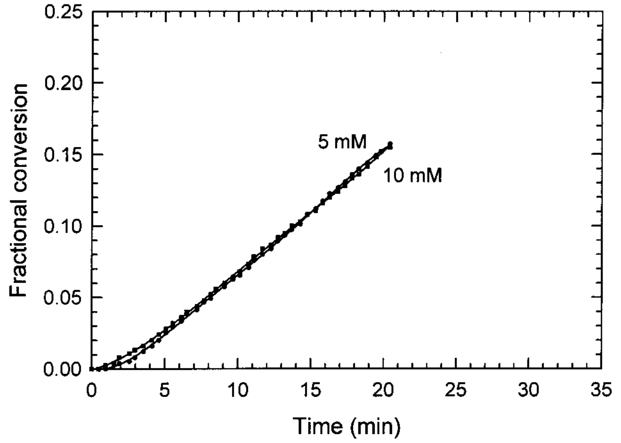

Figure 1. Conversion–time curves for the seeded emulsion polymerization of styrene using 5 and 10 mM SLS. [$Na_2S_2O_8$] = 2 mM; T_r = 50 °C.

Table 2. Entry and Exit Rate Coefficients Calculated by Slope–Intercept Method for the Seeded Emulsion Polymerizations of Styrene ([I] = 2 mM, 50 °C)

surfactant	[E] (mM)	$\bar{n}$	ρ (s^{-1})	k (s^{-1})
SLS	5	0.31	0.0023	0.0026
	10	0.31	0.0023	0.0025
TREM LF-40	2	0.30[a]	0.0018[a]	0.0024[a]
	5	0.29[a]	0.0016[a]	0.0023[a]
	15	0.28[a]	0.0012[a]	0.0017[a]
	20	0.27[a]	0.0011[a]	0.0015[a]
poly(TREM)[b]	2	0.25	0.0017	0.0022
	3.5	0.28	0.0018	0.0021
	5	0.26	0.0017	0.0021
	8	0.27	0.0019	0.0023
	20	0.27	0.0019	0.0021
	25	0.27	0.0019	0.0020
	30	0.26	0.0018	0.0020
	37	0.27	0.0020	0.0024
	41	0.28	0.0021	0.0027

[a] Apparent values, assuming no reactions with TREM LF-40.
[b] Based on monomeric molecular weight of TREM LF-40; the true concentrations are obtained by dividing by 14 (the average number of mers in poly(TREM)).

Effect of Surfactant Concentration. Several parameters affecting the kinetics of the seeded emulsion polymerizations were studied. In all of these experiments, the only change to the systems was in the indicated quantities; all other parameters that could possibly affect the entry rate coefficient were kept constant.

a. SLS. The fractional conversion vs time curves obtained for the seeded emulsion polymerization of styrene using two different SLS concentrations are given in Figure 1. These results show that the reaction kinetics are not obviously affected by the SLS concentration. This result was previously reported by Adams et al.,[9] where they showed that the radical entry rate was independent of surfactant (anionic) coverage within the experimental error. The entry and exit rate coefficients were calculated by the slope–intercept method, and the results are given in Table 2. The values are in the range expected on the basis of prior findings in similar systems.[8]

b. TREM LF-40. The conversion–time curves for the initial part of the seeded emulsion polymerizations using different TREM LF-40 concentrations are shown in Figure 2. These curves show that the rise to steady state (i.e., the time it takes to reach steady state) is more obviously affected than the steady-state rate (slope), the time to reach steady state increasing with increasing TREM LF-40 concentration. For all these reactions, the particle numbers, the monomer–polymer ratios, and the initiator concentrations were the same. Assuming that no additional chemical reactions occur, it can be seen in Table 2 that the apparent steady-state $\bar{n}$ (with 5% experimental error as determined by repeatability studies) decreases slightly with the increasing TREM LF-40 concentration. The entry and exit rate coefficients were estimated from these curves and are also given in Table 2. Both ρ and k appear to decrease. Again, these are only "apparent" values as they cannot account for the influence of TREM LF-40 (copolymerization and chain transfer). Because TREM LF-40 is an allylic monomer, more stable TREM LF-40 radicals (which can be counted as inactive radicals) are formed as a consequence of copolymerization and chain transfer. These can act to decrease the overall reaction rate and may not affect the true values of ρ and k. This, however, cannot be determined definitively by these seeding studies. Nonetheless, the polymerization is slowed with increasing TREM LF-40.

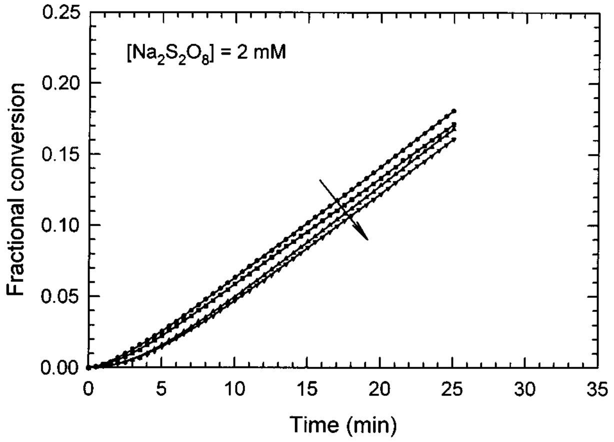

Figure 2. Conversion–time curves for the seeded emulsion polymerization of styrene using 2, 5, 20, and 25 mM TREM LF-40 (increasing in the direction of the arrow). [$Na_2S_2O_8$] = 2 mM; T_r = 50 °C.

c. Poly(TREM). From the results reported above, it was considered important to study the influence of poly(TREM) on the kinetics of the seeded emulsion polymerization, particularly the influence on the entry and exit of the radicals in to and out of the polymer particles. By varying the poly(TREM) concentration (1.43, 1.80, 2.14, 2.64, and 3.57 mM; equivalent to 20, 25, 30, 37, and 41 mM based on the monomeric molecular weight of TREM LF-40) in seeded emulsion polymerizations, the reaction kinetics plotted in Figure 3 were obtained. Although there are some slight differences, there is no obvious trend among the conversion–time curves for the various poly(TREM) concentrations. The entry and exit rate coefficients for all the reactions were estimated and are shown in Table 2. Again, no obvious trend can be seen. The results show that the entry and exit rate coefficients are the same within ±5% for ρ and ±12% for k. Greater uncertainties in such data are typically quoted.[8] These results indicate that the varying surface coverage by this electrosteric stabilizer (within the given experimental range) also has no measurable effect on the radical entry and exit rate coefficients.

The lack of sensitivity of the kinetics to the poly(TREM) level was pursued further by carrying out seeded emulsion polymerizations of styrene using lower

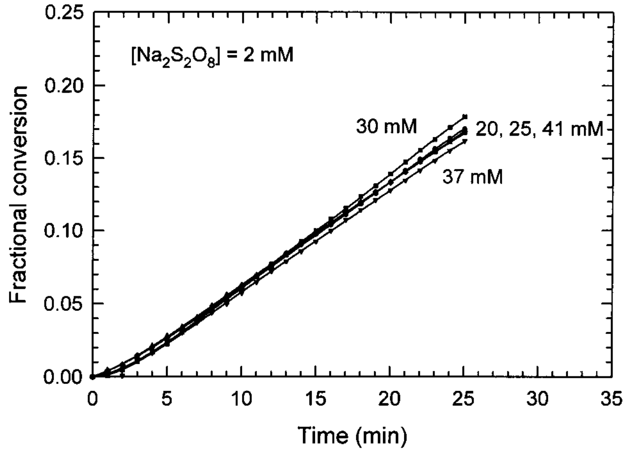

Figure 3. Conversion−time curves for the seeded emulsion polymerization of styrene using varying poly(TREM) concentrations (based on the monomeric molecular weight of TREM LF-40; the true concentrations are 1.43, 1.80, 2.14, 2.64, and 3.57 mM poly(TREM)). [Na$_2$S$_2$O$_8$] = 2 mM; T_r = 50 °C.

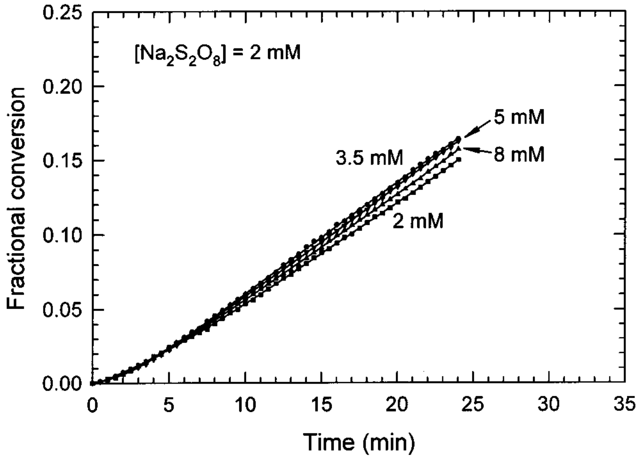

Figure 4. Conversion−time curves for the seeded emulsion polymerization of styrene using varying poly(TREM) concentrations (based on the molecular weight of TREM LF-40; the true concentrations are 0.14, 0.25, 0.36, and 0.57 mM poly(TREM)). [Na$_2$S$_2$O$_8$] = 2 mM; T_r = 50 °C.

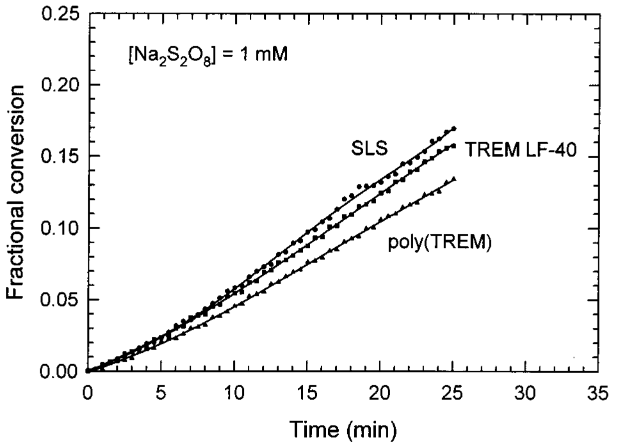

Figure 5. Comparison of conversion−time curves for seeded emulsion polymerizations of styrene using SLS, TREM LF-40, and poly(TREM) [based on the molecular weight of TREM LF-40; the true concentration is 0.72 mM poly(TREM)]. [E] = 10 mM; [Na$_2$S$_2$O$_8$] = 1 mM, T_r = 50 °C.

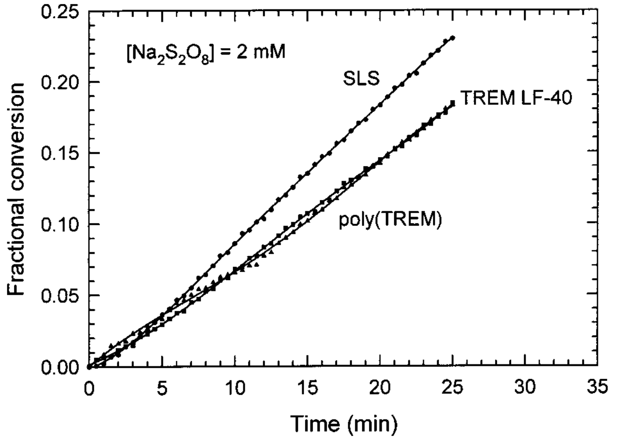

Figure 6. Comparison of conversion−time curves for seeded emulsion polymerizations of styrene using SLS (circles), TREM LF-40 (squares), and poly(TREM) (triangles) [based on monomeric molecular weight of TREM LF-40; the true concentration is 0.72 mM poly(TREM)]. [E] = 10 mM; [Na$_2$S$_2$O$_8$] = 2 mM; T_r = 50 °C.

concentrations of poly(TREM) (0.14, 0.25, 0.36, and 0.57 mM; equivalent to 2, 3.5, 5, and 8 mM based on monomeric TREM LF-40). The conversion−time curves are given in Figure 4, and the estimated entry and exit rate coefficients are also included in Table 2. Again, although variations can be seen, the reaction rates show no obvious trend with the varying poly(TREM) concentration. This is not understood. Reduced rates were expected with increasing poly(TREM). The contribution of the charged "hairy" layer acting as a radical barrier was expected to act to reduce the polymerization rate. Other efforts have reported only modest effects as well.[12]

Comparison of Seeded Emulsion Polymerizations Using the Different Surfactants. The seeded emulsion polymerization kinetics for the three different surfactants SLS, TREM LF-40, and poly(TREM) are given in Figures 5 and 6 at two different initiator concentrations. Using 1 mM Na$_2$S$_2$O$_8$ (Figure 5), the reaction in which poly(TREM) was adsorbed on the seed particles had a slower reaction rate than the reaction using TREM LF-40, which itself was slower than that containing SLS. At the higher initiator concentration, 2 mM (Figure 6), there does not appear to be any significant difference between TREM LF-40 and poly(TREM). Both of these reactions were substantially slower than that containing SLS. Although the results appear to be similar, the explanations for these behaviors for TREM LF-40 and poly(TREM) necessarily differ. As mentioned above, the polymeric surfactant, poly(TREM), is expected to form a "hairy layer" on the particle surface acting as a barrier to the radicals entering the particles, reducing the effective entry rate via the reduced diffusivity of a radical in the adsorbed layer. This leads to slower reaction kinetics. However, for the reactive surfactant, TREM LF-40, the copolymerization and chain transfer reactions to TREM LF-40, which form relatively stable TREM LF-40 radicals, can explain the reduced overall reaction rate. It cannot be ruled out that a "hairy" layer forms in situ during this reaction (by homopolymerization or copolymerization of TREM LF-40). This could affect the entry rate as well. The chain transfer to TREM LF-40 particularly represents a loss of free-radical activity in the reaction system. This can cause the apparent $\bar{n}$ to decrease as well as the entry rate coefficient if the radicals lose their activity inside the particles or at the aqueous phase/particle interface. In general, under similar conditions, $\rho_{\mathrm{SLS}} > \rho_{\mathrm{poly(TREM)}} >$ "ρ_{TREM}". This is due to the chemical

Table 3. Entry and Exit Rate Coefficients for Seeded Emulsion Polymerizations with Varying Initiator Concentrations

[I] (mM)	$\bar{n}$	ρ (s^{-1})	k (s^{-1})
	5 mM SLS		
1	0.27	0.0013	0.0016
2	0.31	0.0023	0.0026
3	0.35	0.0025	0.0014
4	0.36	0.0022	0.0010
5	0.36	0.0028	0.0016
	10 mM TREM LF-40		
1	0.26	0.0014	0.0024
2	0.27	0.0014	0.0022
3	0.29	0.0020	0.0024
4	0.30	0.0015	0.0018
5	0.29	0.0020	0.0024
	10 mM poly(TREM)[a]		
1	0.24	0.0011	0.0025
2	0.26	0.0020	0.0027
3	0.26	0.0013	0.0020
4	0.27	0.0015	0.0023
5	0.31	0.0014	0.0015

[a] Based on monomeric molecular weight of TREM LF-40; the true concentration is 0.72 mM.

Table 4. Number-Average Molecular Weights of Latexes Obtained from the Seeded Emulsion Polymerizations Using SLS, TREM LF-40. and Poly(TREM)

surfactant	[E] (mM)	[I] (mM)	$\bar{M}_n$
SLS	5	1	139 000
		2	132 900
		3	130 000
TREM LF-40	10	1	128 000
		2	124 000
		3	123 000
poly(TREM)	10	1	166 000
		2	148 100
		3	148 000

reactions of TREM LF-40 and the physical effects of poly(TREM).

Based on all the results obtained, the formation of poly(TREM) during the emulsion polymerization of styrene using TREM LF-40 can only be a minor reason to explain the unusual kinetics of the conventional emulsion polymerization of styrene using TREM LF-40. The main reason still lies in the chemical reactions of TREM LF-40, which decrease the overall reaction rate. These occur primarily at the surface of the particles where the concentration of TREM LF-40 is relatively high and increases with increasing TREM LF-40 concentration. The latter causes the rate to become increasingly affected, which in turn has the effect of lowering the dependency of the rate on the surfactant concentration.

Effect of Initiator Concentration. It is expected that the entry rate coefficient will increase with increasing initiator concentration, while the exit rate coefficient should remain essentially constant.[8] The kinetics of the seeded emulsion polymerization of styrene using SLS, TREM LF-40, and poly(TREM) at five different initiator concentrations (1, 2, 3, 4, and 5 mM) were measured. The reaction rate increased with increasing [I] in all cases. The estimated entry and exit rate coefficients for these reactions are given in Table 3. With increasing [I], the rate of generation of free radicals increases, leading to an increasing entry rate (ρ), which in turn leads to an increase in $\bar{n}$. For the seeded emulsion polymerizations using poly(TREM), there is considerable scatter in the data, although the entry rate coefficient generally increases with increasing initiator concentration. The increasing rate is better reflected in $\bar{n}$. These results indicate that at a given initiator level the rate of polymerization is reduced by the presence of TREM LF-40 or poly(TREM) as compared to SLS.

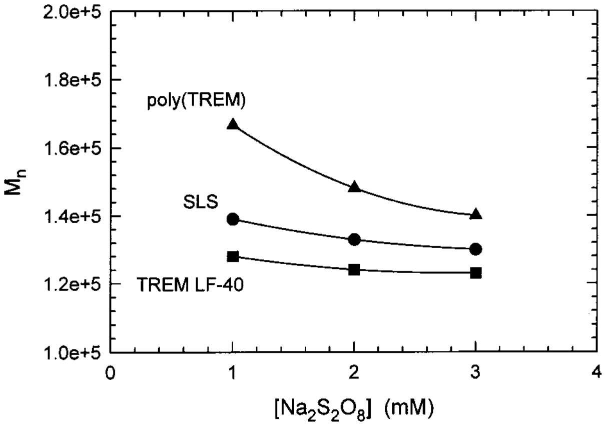

Figure 7. Number-average molecular weight of polystyrene latexes as a function of the initiator concentration resulting from seeded emulsion polymerizations using 5 mM SLS, 10 mM TREM LF-40, and 0.72 mM poly(TREM) (equivalent to 10 mM based on the molecular weight of TREM LF-40).

Molecular Weights of Latexes Prepared by Seeded Emulsion Polymerization. In general, the radical entry rate will directly affect the average molecular weight of the polymer formed in an emulsion polymerization where termination is an important chain-stopping event. In a system where chain transfer to monomer and radical desorption dominates, this would not be the case. In these experiments, an increased entry rate is expected to reduce the molecular weight particularly since the reactions are carried out to over 80% conversion where the gel effect (reduced termination) plays a significant role in the last stages of the reaction. Indeed, that is what is seen by the results reported in Table 4 and Figure 7. Not only is the number-average molecular weight ($\bar{M}_n$) reduced by increasing the initiator concentration for each surfactant as expected, but it is reduced further by using TREM LF-40 and increased by using poly(TREM) relative to the results obtained for SLS. Both of these results are readily understood on the basis of the proposed mechanisms of these polymerizations. Chemical reactions, primarily chain transfer to TREM LF-40 at the surface of the particles, lead to the reduced molecular weight. The lower entry rate caused by the "hairy" poly(TREM) layer brings about the increased molecular weight.

Conclusions

The presence of either TREM LF-40 or poly(TREM) was found to decrease the rate of seeded emulsion polymerization of styrene relative to parallel control experiments using SLS as the stabilizer. The rate of polymerization decreased with increasing TREM LF-40 concentration but was relatively constant over the range of poly(TREM) concentrations employed. The slope−intercept method was applied to the conversion vs time data to estimate the pseudo-first-order entry (ρ) and exit (k) rate coefficients. The decrease in polymerization rate (decreasing apparent values of ρ) in the presence of increasing amounts of TREM LF-40 was attributed to copolymerization and chain transfer to the reactive surfactant. The decrease in reaction rate (including $\bar{n}$ and ρ), noted when poly(TREM) was used as surfactant, was explained by the reduced diffusivity of radicals through the "hairy" layer created by adsorption of the electrosteric stabilizer on the surface of the particles. The molecular weights of the resulting polymers provided supporting evidence for these mechanisms. The number-average molecular weights were the highest for the final latexes polymerized with adsorbed poly(TREM) and lowest for those with adsorbed TREM LF-40, the SLS system producing intermediate values. The former corresponds to a reduced rate of radical entry (less frequent termination), while the latter is consistent with chain transfer occurring at the particle surface. For all cases, the molecular weights of the latexes decreased with the increasing initiator concentration, as expected. These results are consistent with those found for the conventional emulsion polymerizations using TREM LF-40 and poly(TREM), giving supporting evidence for the role of TREM LF-40 and poly(TREM) in these reactions.

These results help to explain why the rate of polymerization was not found to be proportional to the first power of the number of particles ($R_p \propto N_p^{1.0}$) in previous conventional emulsion polymerizations of styrene employing varying amounts of TREM LF-40 ($R_p \propto N_p^{0.7}$) as surfactant.[18] The reduced rate caused by the reactions at the surface of the particles acted to lower the dependencies of the rate of polymerization on the TREM LF-40 concentration.

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Supporting Information Available: Mathematical description of the "slope−intercept" technique to obtain ρ and k from conversion vs time data. This material is available free of charge via the Internet at http://pubs.acs.org.

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