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Emulsion Polymerization of Styrene Using a Reactive Surfactant and Its Polymeric Counterpart: Kinetic Studies

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ABSTRACT: Emulsion polymerizations of styrene using the reactive surfactant sodium dodecyl allyl sulfosuccinate (TREM LF-40) and its polymeric counterpart, poly(TREM), were studied. The critical micelle concentrations (cmc) and the adsorption behaviors on polystyrene latex particles were determined. The polymerization kinetics obtained via reaction calorimetry showed that the emulsion polymerization of styrene using the reactive surfactant behaved similarly to those reported for the conventional surfactant sodium lauryl sulfate (SLS) in that the rate of polymerization (R_p) profiles showed the same three distinct regions: a rapid rise in rate, attributed to micellar nucleation (interval I); a moderate rise in rate to a maximum where droplets disappear, attributed to homogeneous nucleation (stage 2); and the decreasing rate period (interval III). However, with varying TREM LF-40 concentration (constant initiator concentration), R_p was not found to be proportional to the first power of N_p as reported for the SLS system, but 0.7 instead (i.e., $R_p \propto N_p^{0.67}$). In contrast, by varying the initiator concentration, the kinetics were found to have the same dependencies as the conventional surfactant ($R_p \propto N_p^{1.0} \propto [I]^{0.4}$). These differences are attributed to the participation of the surfactant in the reaction. The kinetics using poly(TREM) differed from those of the reactive counterpart in several ways. The R_p profiles indicated a longer homogeneous nucleation stage 2 in comparison to interval I. Larger (fewer) particles were produced for equivalent weights of the surfactants. This was expected. Although R_p was found to be proportional to the first power of N_p, the dependencies on the surfactant and initiator concentrations varied depending on concentration of the component held constant ($R_p \propto N_p^{1.0} \propto [E]^{0.2-0.5}$ and $R_p \propto N_p^{1.0} \propto [I]^{0.4-0.8}$). The lower dependencies on the surfactant concentration and higher dependencies on the initiator concentration are attributed to the ionic strength and the longer nucleation period.

Introduction

Emulsion polymerization is one of the most important techniques for preparing polymers from an industrial point of view. However, the use of conventional surfactants such as sodium lauryl sulfate (SLS) can have negative effects on product properties due to their physical adsorption on the polymer particles. Surfactants can migrate to the surface of a latex coating and can desorb from the latex particle surface under high shear, causing destabilization.[1−3] Several methods can be used to eliminate such disadvantages. In surfactant-free emulsion polymerization, the latex particles are stabilized by the sulfate end groups derived from the persulfate initiator.[4,5] However, because of the relatively low particle surface charge density, a significant amount of coagulum can form during the reaction by this method, particularly at high solids. Functional monomers can copolymerize with the monomer and contribute to the hydrophilic−lipophilic balance on the latex particles,[6−8] replacing the surfactant. However, because of their high solubility in water, large amounts of water-soluble oligomers are often formed, which is not desirable. A more promising method is to use reactive surfactants, which can ensure the chemical incorporation of the surfactant into the latex particles during the course of the polymerization.[9−17] The desorption of the surfactant from the latex particle surface or migration in the polymer film is eliminated by chemical incorporation of the surfactant into the polymers.

Reactive surfactants can be an initiating moiety (inisurf), a moiety capable of chain transfer (transurf), or a group capable of copolymerization during the free-radical polymerization (surfmer).[9−17] The most promising possibility lies in the surfmers. Anionic surfmers with sulfate or sulfonate headgroups, cationic surfmers, and nonionic surfmers have been synthesized and applied in emulsion polymerizations. For example, allylic monomers such as sodium 10-undecenoate[18] and allyldimethyldodecylammonium bromide[19] have been shown to exhibit considerable polymerizability at concentrations above their cmc's. Although the application of reactive surfactants and their copolymerization behavior have been presented,[20] fundamental studies of their kinetics and mechanism in emulsion polymerization are still scarce.

Polymeric surfactants have also been widely used in emulsion polymerization.[21−25] A general review on this topic has been published by Piirma.[26] Also, a review of polymeric surfactants and their application in polymerization and coatings has been presented by Bouvy.[27] Polymeric surfactants have relatively low cmc's, and they provide stability by a steric repulsion force between interacting particles. This gives the latex excellent stability against high electrolyte concentrations, freeze−thaw cycling, and high shear rates. When polymeric surfactants also have ionic groups in their molecular structure, electrostatic and steric stabilization effects are combined being referred to as electrosteric stabilization.[21] Understanding the role of this kind of polymeric surfactant in emulsion polymerization is of particular interest.

This paper focuses on the kinetics of the emulsion polymerization of styrene using the reactive surfactant

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TREM LF-40 and its polymeric counterpart, poly(TREM).

Experimental Section

Materials. Styrene monomer (Aldrich) was washed with 10 wt % aqueous NaOH (Fisher Scientific) followed by deionized water and distilled under vacuum prior to use. Buffer ($NaHCO_3$, Aldrich) and initiator ($Na_2S_2O_8$, FMC Corporation) were analytical grade. TREM LF-40 (sodium dodecyl allyl sulfosuccinate) was used as received (Cognis Corp.). Deionized (DI) water was used throughout. Poly(TREM) was prepared by solution polymerization of TREM LF-40 (28.08 g) in DI water (360 g), with $NaHCO_3$ (10 mM) as buffer and $Na_2S_2O_8$ (16 mM) as initiator. The reaction was carried out at 60 °C for 12 h and 90 °C for an additional 9 h to obtain the highest reaction conversion and decompose the initiator completely. This was used as is in subsequent emulsion polymerizations.

Emulsion Polymerization Procedures. Emulsion polymerizations were carried out in the Mettler RC1 reaction calorimeter equipped with a 1 dm^3 MP10 reactor, pitched blade impeller, and baffle. The reactor was first charged with 420.0 g of water, buffer ($NaHCO_3$, 4−10 mM), and surfactant (20−50 mM), followed by 218.4 g of styrene monomer. The reactor was flushed with nitrogen (Zero grade, Airgas/JWS Technologies, Inc.) for about 20 min and sealed. The temperature was set at 25 °C and a calibration was performed, and then the temperature was ramped to the reaction temperature (60 °C) over 10 min and a second calibration was performed. Details on use of the RC1 have been given previously.[28] The initiator ($Na_2S_2O_8$) solution (4−10 mM) was then added to start the reaction. A sample was taken by syringe at the maximum in the heat of reaction curves for particle size analysis along with the final latex. When the reaction was completed (conversion > 95%), an aqueous solution (1 wt %) of hydroquinone (Aldrich) was added to the latex and two more calibrations were performed at the reaction temperature (60 °C) and 25 °C. The calibrations were necessary for determining the heat transfer coefficients and heat capacities needed for evaluating the raw data. Continuous heat of reaction vs time curves (data acquired every 2 s) were obtained directly from the RC1 evaluation software, and the polymerization rate was calculated using eq 1:

$$R_p = \frac{Q_r}{V_{H_2O}\Delta H} = KQ_r \tag{1}$$

where the heat of the reaction Q_r (J/s) can be used directly to obtain the reaction rate, R_p (mol/dm^3/s). V_{H_2O} is the volume of DI water charged (dm^3), and ΔH is the heat of polymerization of styrene (J/mol). K is a constant and since there is only a constant difference between R_p and Q_r; R_p can be represented by Q_r.

Analytical Methods. The number-average molecular weight of the poly(TREM) was measured by vapor pressure osmometry (VPO)[29] using a Knauer VPO (Utopia Instrument Company). Water was chosen as the solvent, while NaCl was used for calibration of the instrument. Poly(TREM) solution concentrations were varied from 27 to 82 g/kg. Measurements were made at 40 °C.

The critical micelle concentrations (cmc) of the surfactants were determined by surface tension measurements on aqueous solutions as measured by the maximum bubble pressure method (SensaDyne surface tensiometer 6000, Chem-Dyne Research Corp.). Adsorption isotherms on a polystyrene latex were determined by applying the serum replacement technique.[30] The surfactant concentrations were measured by refractive index (Fisher Scientific Co.). The latex used in this study was a monodisperse, 92 nm polystyrene latex (LS 1039E, Dow Chemical Co.), which was initially cleaned by serum replacement.

The presence/absence of carbon−carbon double bonds in TREM LF-40 and the poly(TREM) was measured by FTIR (Mattson Sirius model 100 FTIR spectrophotometer) and bromine titration as described in detail elsewhere.[15]

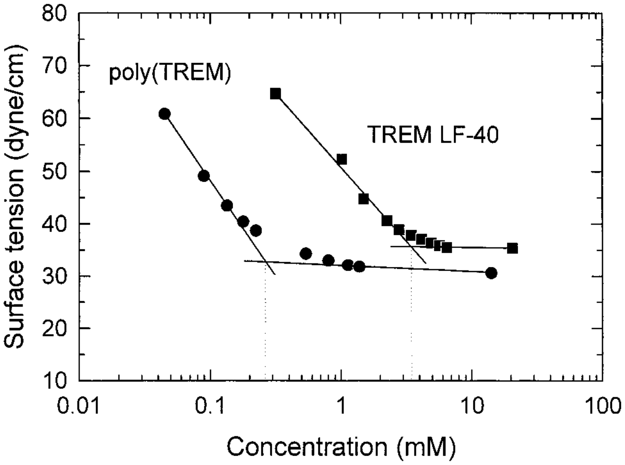

Figure 1. Surface tension vs aqueous surfactant concentration for TREM LF-40 and poly(TREM) at room temperature.

Monomer conversion was independently determined by gas chromatography (GC, Hewlett-Packard 5890) and gravimetry. The reaction rates were obtained from the Mettler RC1. The continuous conversion vs time curves of the reactions were obtained by integration of the R_p vs time curves.

Particle sizes distributions of the latexes were measured by capillary hydrodynamic fractionation (CHDF 1100, Matec Applied Sciences) and, in some cases, by transmission electron microscopy (TEM, Philips EM 400).

Results and Discussion

Molecular Weight of Poly(TREM). On the basis of the VPO data, the molecular weight (M_n) of poly(TREM) was 6000 ± 300 g/mol, which means that each poly(TREM) molecule is made up of an average of about 14 units of TREM LF-40 (MW = 428 g/mol).

Cmc's and Adsorption Isotherms. The surface tensions of aqueous solutions of TREM LF-40 and poly(TREM) are illustrated in Figure 1 as a function of concentration (C). The break points of the curves represent the cmc values. From these data, the cmc's are estimated to be 3.2 mM for TREM LF-40 and 0.27 mM for poly(TREM). As a reference, the cmc of sodium lauryl sulfate, a common surfactant used in emulsion polymerization, is about 7 mM.

The results of the adsorption isotherm measurements of TREM LF-40 and poly(TREM) on polystyrene are given in Figure 2. The isotherm represents the amount of surfactant adsorbed per unit area (N_a) of the polymer particles (polystyrene) as a function of the aqueous phase surfactant concentration (C_a). Figure 2 indicates that after poly(TREM) saturated the surface of the polymer particles (plateau), a second rise occurred, indicating the formation of a thicker layer resulting from rearrangement and/or multilayer adsorption. This is not unusual for a polymeric stabilizer.

The saturation areas (a_s) were calculated using the linear Langmuir equation:

$$\frac{1}{N_a} = a_s + \frac{a_s}{b}\frac{1}{C_a} \tag{2}$$

where b is the ratio of adsorption to desorption rate constants. The estimated values of a_s are 55.4 Å^2/molecule for TREM LF-40 and 478 Å^2/molecule for poly(TREM). These results indicate that poly(TREM) as a

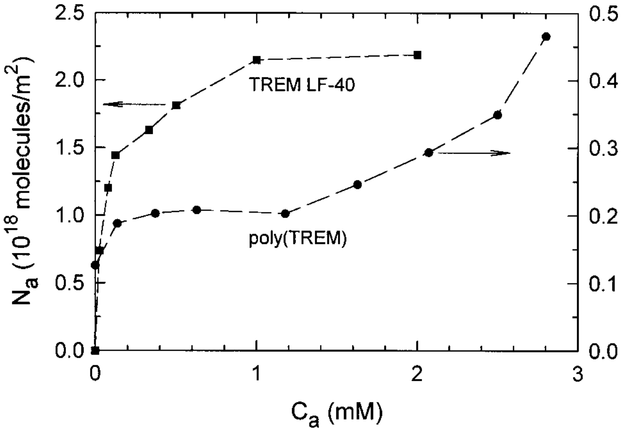

Figure 2. Adsorption isotherms of TREM LF-40 and poly(TREM) on polystyrene latex particles at room temperature.

Table 1. Results of Bromine Titrations To Determine C=C Concentration in TREM LF-40 and Poly(TREM)

surfactant	surfactant concn (mM)	C=C concn (mM)
TREM LF-40	0.18	0.18
poly(TREM)[a]	0.18	~0.01

[a] Concentration based on mass of TREM in poly(TREM).

surfactant is more crowded on the polystyrene particles. The latter can be noted on the basis of the value of a_s calculated for poly(TREM) in terms of monomeric TREM (34 Å^2/molecule) rather than the value for the poly(TREM) (478 Å^2/molecule) itself. The poly(TREM) molecules likely form loops and/or tails extended from the surface of the polymer particles.

The carbon−carbon double bonds present in the TREM LF-40 monomer can be detected by FTIR at 992 and 927 cm^{-1}. The FTIR spectra of H-TREM (hydrogenated TREM LF-40) and poly(TREM) show no peaks at 992 and 927 cm^{-1}, while the peaks are obvious in the spectrum for TREM LF-40. These results indicate that no measurable quantity of double bonds are present in the poly(TREM). The presence/absence of these double bonds was also examined by bromine titration. A calibration curve was generated from the titration of solutions having various known TREM LF-40 concentrations. The results given in Table 1 show that the residual double-bond concentration in poly(TREM) was insignificant. Thus, both the FTIR and bromine titration results show that the concentration of C=C bonds in poly(TREM) was below the detection limits for each method (5% for FTIR, 1% for bromine titration).

Emulsion Polymerization. a. TREM LF-40 as Surfactant. In the first series of styrene emulsion polymerizations, TREM LF-40 was used as surfactant. The variation in the initiator and TREM LF-40 concentrations are given in Table 2. The results obtained by first varying the surfactant concentration at a fixed persulfate concentration (4 mM) are reported in Figure 3. Heat of reaction and conversion vs time curves are presented. The most obvious global observation is that the reaction rate increased with increasing surfactant concentration, this being qualitatively the same as expected using conventional surfactants. However, this is the opposite of what was found in the emulsion polymerization of vinyl acetate using TREM LF-40 as surfactant, where the rate of polymerization decreased with increasing surfactant concentration.[14] A second observation is that the shapes of all the rate curves are similar. The rates increased rapidly at first and then more slowly with a nearly constant slope and then passed through a maximum. The rates subsequently decreased and then exhibited a shoulder which decreased in magnitude with increasing surfactant. This shoulder is attributed to the gel effect, which typically becomes more prominent with increasing particle size (increasing $\bar{n}$, average number of free radicals per particle). The shoulder is followed by a decrease to a low rate as the monomer concentration drops to a low level. Figure 4 shows the rate of polymerization graphed as a function of the fractional conversion. Here it becomes obvious that these phenomena occur at the same conversions: the first transition occurs at about 2% conversion, the maximum occurs at 42−44% conversion, and the gel effect in the region of 75−85% conversion. This agrees qualitatively with the results reported previously by Varela de la Rosa et al. for emulsion polymerizations of styrene conducted at 50 °C using

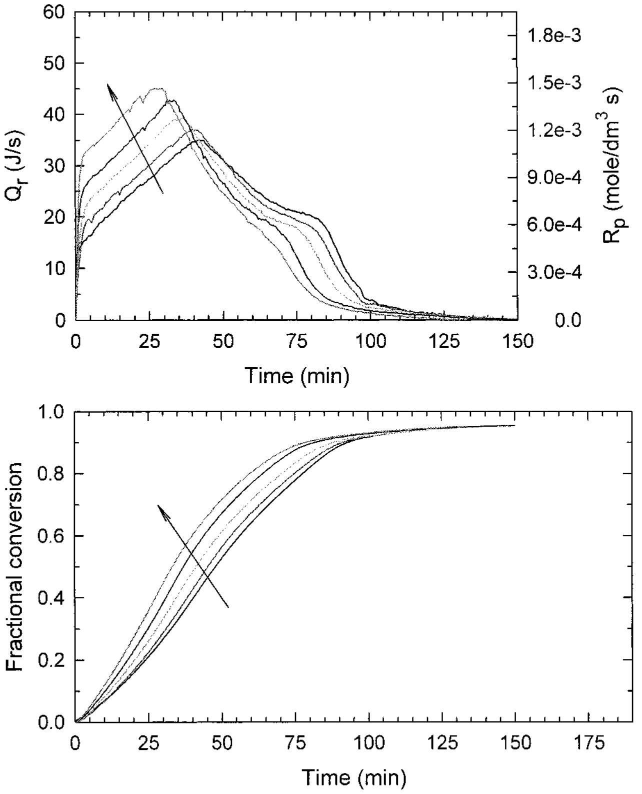

Figure 3. Kinetics of the emulsion polymerization of styrene using TREM LF-40 as the surfactant at 4 mM [$Na_2S_2O_8$]. TREM LF-40 concentration increases in the direction of the arrow: 20, 25, 30, 40, and 50 mM. (top) Heat of reaction vs time. (bottom) Conversion vs time. T_r = 60 °C.

Table 2. Variation in Initiator and TREM LF-40 Concentrations in Emulsion Polymerizations of Styrene at 60 °C: Resulting Particle Size and Number of Particles

reaction	[I] (mM)	[TREM LF-40] (mM)	D_v (nm)	D_w (nm)	PDI	N_p ($\times10^{-18}$) (/dm^3 H_2O)
T-I4-S20	4	20	88.5	94.8	1.154	1.29
T-I4-S25		25	86.5	91.6	1.148	1.39
T-I4-S30		30	84.0	90.1	1.165	1.52
T-I4-S40		40	81.2	87.5	1.156	1.68
T-I4-S50		50	77.6	82.7	1.145	1.92
T-I5-S20	5	20	89.0	95.1	1.153	1.27
T-I5-S30		30	84.0	90.2	1.152	1.52
T-I5-S40		40	77.6	83.8	1.168	1.92
T-I8-S20	8	20	83.1	88.2	1.146	1.57
T-I8-S30		30	76.7	81.9	1.148	1.99
T-I8-S40		40	73.4	79.5	1.163	2.27

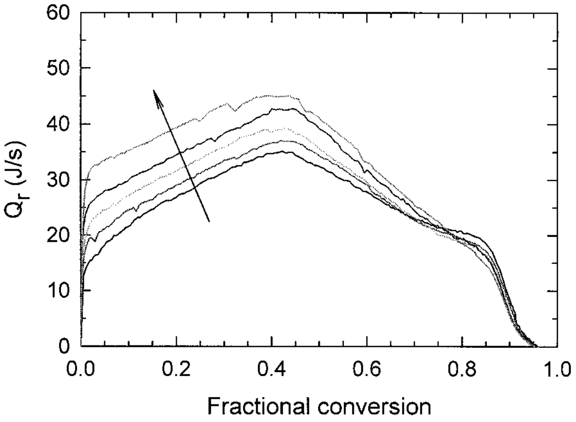

Figure 4. Heat of reaction vs conversion curves for the emulsion polymerization of styrene using TREM LF-40 as the surfactant at 4 mM [$Na_2S_2O_8$]. TREM LF-40 concentration increases in the direction of the arrow: 20, 25, 30, 40, and 50 mM. T_r = 60 °C.

similarly varying concentrations of sodium lauryl sulfate as surfactant and potassium persulfate as initiator.[31] In the latter, the stages of the reaction were described as follows. The initial rapid increase in the rate is brought about by micellar nucleation, which ends at a low conversion with the disappearance of the micelles; this is referred to as interval I, as in the classical description. The next stage is characterized by a slower increase in rate which is brought about by a further increase in the number of particles through homogeneous nucleation. This is referred to as stage 2 rather than the classical interval II, which is typically characterized as having a constant rate and number of particles. After the maximum, the rate decreases in interval III, coinciding with a decreasing monomer concentration and a constant number of particles. These polymerizations with TREM LF-40 are believed to follow the same mechanism by virtue of the strong similarity of the rate behavior to that reported in the prior work. It should be noted that the overall increase in rate with increasing TREM LF-40 concentration correlates qualitatively with an increasing number of particles as reported in Table 2. This is normally what would be expected. However, it should also be noted that, in the prior work with vinyl acetate, the opposite trend was reported where the overall rate of polymerization *decreased* with the *increasing* number of particles brought about by the increasing TREM LF-40 concentration. This unexpected behavior was finally attributed to extensive chain transfer to TREM LF-40 occurring at the surface of the latex particles, as proven by competitive growth experiments.[14]

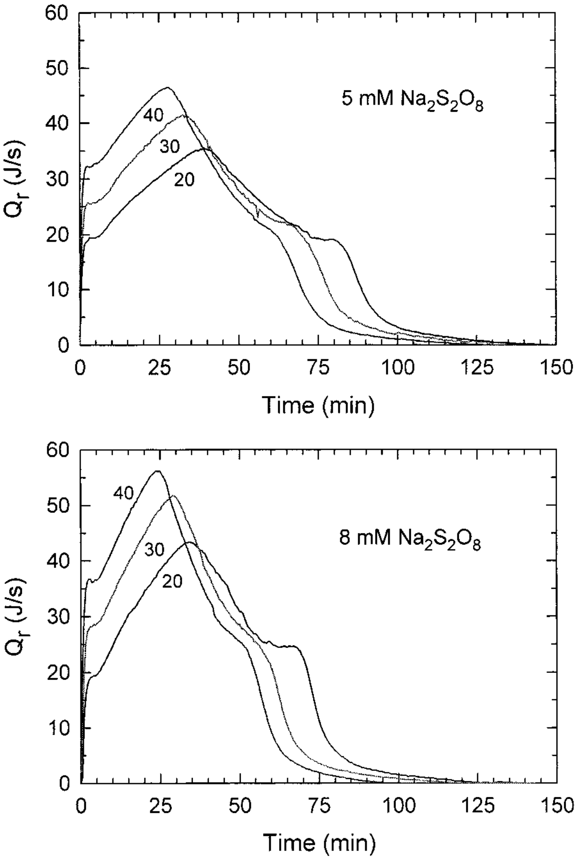

Figure 5. Heat of reaction vs time curves for the emulsion polymerization of styrene using TREM LF-40 as the surfactant at 20, 30, and 40 mM TREM LF-40 concentrations; 5 mM (top) and 8 mM (bottom) [$Na_2S_2O_8$]. T_r = 60 °C.

For the two higher initiator concentrations (5 and 8 mM), similar kinetics can be seen as shown in Figure 5 where the rate of polymerization is given as a function of time for varying TREM LF-40 concentrations. However, a somewhat unusual and interesting phenomenon was seen in these kinetics that was not seen at the lower initiator concentration. The first transition seems to be accompanied by a brief near constant reaction rate period just after the initial quick rise in the heat of reaction (attributed to micellar nucleation) (see Figure 5). This was not seen in similar reactions employing SLS as the emulsifier.[31] Some possible explanations are that (1) in the transition from micellar ("fast" nucleation) to homogeneous ("slow" nucleation) nucleation, the reactions of TREM LF-40 at the surface of the particles slows the rate of polymerization counteracting the increase in the number of particles, and (2) during this period the particles are not very stable and some limited aggregation takes place, reducing the existing particle number and counteracting the continued nucleation of particles (i.e., a constant number of particles exists in this period). This could be caused by the increased ionic strength brought about by the increased initiator concentration or to the formation of poly(TREM) or styrene/TREM LF-40 copolymer during the initial stages of the emulsion polymerization, which might also have some tendency to destabilize the particles (bridging flocculation). Without further detailed study of this region, no conclusive explanation can be offered. Nonetheless, the behaviors at these two initiator concentrations are otherwise similar, and the same nucleation mechanisms are considered to dominate the kinetics as described above.

The particle sizes of the latexes sampled at the rate maximum and at the end of each reaction were also measured by CHDF and the numbers of particles calculated from D_v (volume-average diameter). The two numbers agreed within the error of the measurement, indicating no nucleation had occurred beyond the disappearance of the monomer droplets. The final values are reported in Table 2. The results show that the particle size decreased with increasing TREM LF-40 concentration; i.e., the particle number increased, as expected.

Although both the reaction rate and the particle number increased with increasing TREM LF-40 concentration, further quantitative comparisons are warranted in terms of the dependencies of R_p and N_p on

Table 3. Kinetic Parameters Obtained from the Emulsion Polymerization of Styrene Using TREM LF-40 as Surfactant

$[Na_2S_2O_8]$ (mM)	[TREM LF-40] (mM)	$Q_r(R_p) \propto [E]^A$ A	$N_p \propto [E]^B$ B	$Q_r(R_p) \propto N_p^C$ C
4	20−50	0.28	0.42	0.67
5	20−40	0.39	0.58	0.67
8	20−40	0.38	0.54	0.70

$[Na_2S_2O_8]$ (mM)	$\bar{n}$ at $R_{p,max}$ [E] = 20 mM	[E] = 30 mM	[E] = 40 mM
4	0.288	0.268	0.260
5	0.281	0.271	0.246
8	0.283	0.276	0.252

the surfactant and initiator concentrations to further understand the kinetics and the mechanism of these reactions. The relationships between Q_r (R_p), N_p, and the surfactant concentration ([E]) and also the average radical numbers per particle ($\bar{n}$) are summarized in Table 3. First note that the rate of polymerization (maximum) is not proportional to the first power of the number of particles, but rather it is the 0.7 power in all three cases. This is unusual for the emulsion polymerization of styrene, which typically follows closely the Smith−Ewart description ($R_p \propto N_p^{1.0}$).[31] Here, the dependency of the rate on the TREM LF-40 concentration is less than the dependency of the number of particles. In addition, the latter dependencies approach 0.6 (the Smith−Ewart value) for the two higher initiator concentrations but are lower for the 4 mM persulfate level. This behavior was initially unexpected given the general trend of the kinetic data and the low reactivity of the surfactant with styrene ($r_1 = 13$, $r_2 = 0.5$).[15] Nonetheless, these results would seem to point to some effect of TREM LF-40 on the reaction kinetics other than its role as a surfactant. If the primary locus for copolymerization of the reactive surfactant is at the particle surface, then it is expected that the copolymerization rate will be increasingly affected as the particles become smaller, i.e., increasing reaction owing to the increasing surface-to-volume ratio. It is expected that the reactive surfactant would increasing slow the rate with increasing concentration. This could be caused by copolymerization and/or degradative chain transfer to the allylic monomeric surfactant. An extreme case of this was seen in the emulsion polymerization of vinyl acetate.[32]

The values of $\bar{n}$ obtained at $R_{p\ max}$ are similar and well below case 2 conditions ($\bar{n} = {}^1/_2$). This is not surprising with such small particles. Some might attribute the reported R_p dependency on N_p to this occurrence, but this is not considered likely in this case since when the initiator concentration was varied at a constant surfactant level the dependency was 1.0, as reported below.

The kinetic data presented in Figures 4 and 5 can be reorganized to illustrate the effect of the initiator concentration on the reaction rate, as shown in Figure 6. Q_r vs time curves at 20, 30, and 40 mM TREM LF-40 concentrations are represented. With increasing initiator concentration, both reaction rate and particle number (Table 2) increased. Note, however, that the slopes of the Q_r vs time curves after the first transition are no longer parallel going from 5 to 8 mM initiator. This would indicate an increased rate of homogeneous nucleation, which might be expected for an increased rate of radical production. In contrast to the preceding results, at a fixed surfactant concentration, the rate of polymerization is indeed proportional to the first power of the number of particles as would normally be expected from Smith−Ewart theory ($R_p \propto N_p^{1.0}$). Plus, the dependencies on the initiator concentration follow the theory ($R_p \propto [I]^{0.4}$) for the two higher surfactant concentrations while it is slightly lower at 20 mM TREM LF-40 (0.33). The dependencies of R_p and N_p on the initiator concentration are summarized in Table 4.

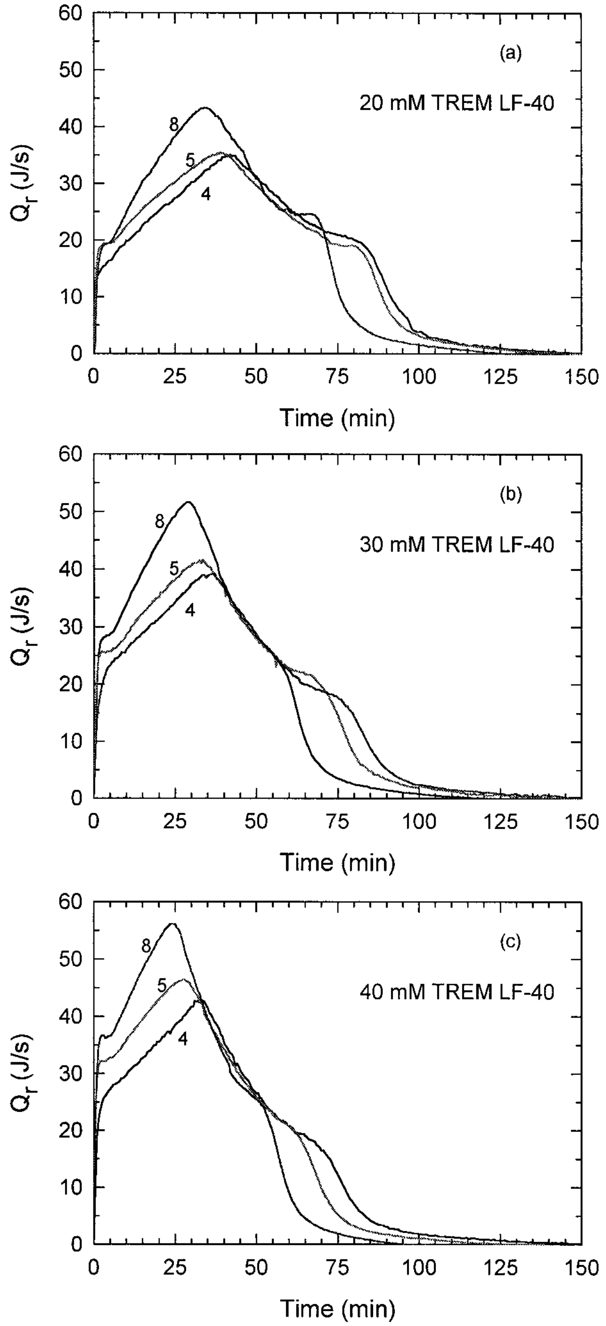

Figure 6. Heat of reaction vs time curves for the emulsion polymerization of styrene using TREM LF-40 as the surfactant at (a) 20, (b) 30, and (c) 40 mM [E] and different initiator concentrations. T_r = 60 °C.

The reason for these atypical kinetics is not obvious. Although copolymerization and chain transfer to TREM LF-40 can occur in all phases including the particle/water interface, the relative contributions need to be investigated. The fact that variation in the initiator concentration at a fixed TREM LF-40 concentration

Table 4. Dependencies Obtained from the Kinetics of Emulsion Polymerization of Styrene Using TREM LF-40 as Surfactant

[TREM LF-40] (mM)	[$Na_2S_2O_8$] (mM)	$Q_r(R_p) \propto [I]^A$ *A*	$N_p \propto [I]^B$ *B*	$Q_r(R_p) \propto N_p^C$ *C*
20	4−8	0.32	0.33	1.02
30		0.41	0.41	1.00
40		0.40	0.43	1.07

leads to Smith−Ewart kinetics may point to the aqueous phase as being largely responsible, since the extent of the particle/water interface increases with increasing initiator concentration, and yet the kinetics are unaffected in a relative sense. This is explored in more depth in separate publication.[33]

b. Poly(TREM) as Surfactant. In the second series of styrene emulsion polymerizations, poly(TREM) was used as the stabilizer. A polyelectrolyte, such as poly(TREM), can act as both a steric and an electrostatic stabilizer in emulsion polymerization. It has been shown that a polymeric surfactant can decrease the entry and exit rates of radicals to and from the latex particles.[20] Therefore, its effects on the emulsion polymerization of styrene compared to TREM LF-40 are of interest. The variations in the initiator and poly(TREM) concentrations are given in Table 5, along with the final particle sizes and numbers of particles. Note that the concentration of poly(TREM) is given based on the poly(TREM) molecular weight, while the designations for each experiment indicate the equivalent millimolar concentration based on the number of mers of TREM LF-40 (e.g., P-I5-S20: poly(TREM); 5 mM initiator; 1.43 mM surfactant (i.e., 20 mM, based on the monomeric molecular weight of TREM LF-40)). The polymerization kinetics are presented in Figures 7 and 8. The similarities between these results and those presented for TREM LF-40 include (1) increasing reaction rate with increasing stabilizer concentration, (2) rate maxima occurring in the 42−44 wt % conversion region, and (3) in some cases (primarily at 8 and 10 mM initiator concentrations), the appearance of a short, apparently constant rate period after the initial rapid increase upon injection of the initiator. Although the shape of the curves are similar, there are some important differences: (1) the magnitude of the initial increase in rate was reduced with a corresponding increase in the slower rise to the rate maximum; (2) the slope after the first transition increased with increasing poly(TREM), while it was relatively constant using TREM LF-40; and (3) the rate profiles became more similar with increasing initiator concentration, i.e., the dependence on the initiator concentration decreased, while it was relatively constant for TREM LF-40. These are particularly apparent at the higher initiator concentrations. The first difference is indicative of a significant change in the nucleation mechanism between the two stabilizers. Using poly(TREM) as the surfactant apparently resulted in a much shorter micellar nucleation period and a longer homogeneous nucleation period. These results are consistent with the notion that a polymeric surfactant produces fewer micelles compared to a conventional surfactant.

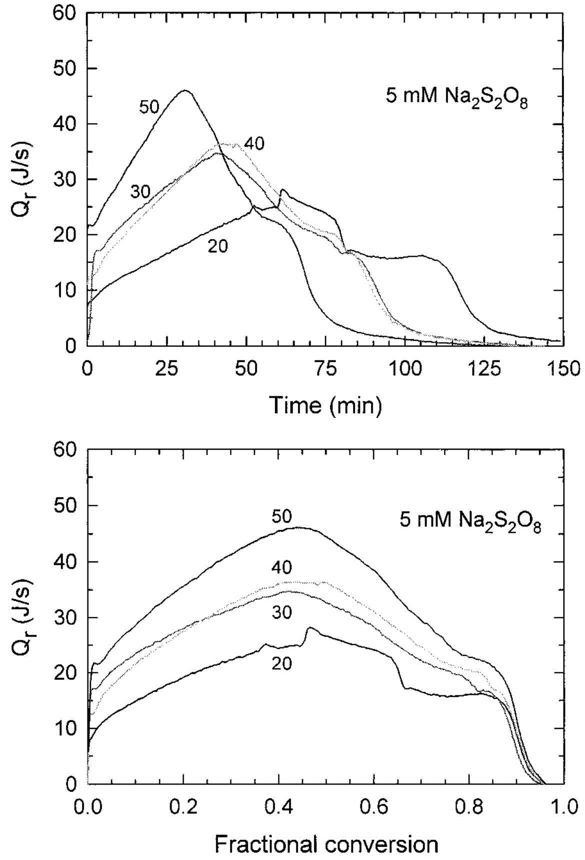

Figure 7. Kinetics of the emulsion polymerization of styrene using poly(TREM) as the surfactant at 5 mM [I] and different poly(TREM) concentrations. Heat of reaction vs time (top) and heat of reaction vs conversion (bottom). T_r = 60 °C.

The final particle sizes of these latexes were measured by CHDF. The results given in Table 5 show that for the 5 and 8 mM $Na_2S_2O_8$ concentrations the particle size decreased (N_p increased) with increasing poly(TREM) concentration. However, at 10 mM $Na_2S_2O_8$, the particle size remained relatively constant at about 80 nm despite the increasing poly(TREM) concentration. One possible reason for this is the effect of the ionic strength. With

Table 5. Particle Size (CHDF) of PS Latexes Prepared with Different Initiator and Poly(TREM) Concentrations

reaction	[$Na_2S_2O_8$] (mM)	[poly(TREM)] (mM)	D_v (nm)	D_w (nm)	PDI	N_p ($\times 10^{-18}$) (dm^{-3} H_2O)
P-I5-S20	5	1.43	96.4	99.5	1.064	1.00
P-I5-S30		2.14	88.8	91.2	1.066	1.28
P-I5-S40		2.85	86.9	89.9	1.056	1.37
P-I5-S50		3.56	82.3	86.2	1.078	1.46
P-I8-S20	8	1.43	85.0	88.1	1.051	1.64
P-I8-S30		2.14	81.8	85.0	1.062	1.77
P-I8-S40		2.85	79.7	82.8	1.062	1.84
P-I10-S20	10	1.43	81.6	84.8	1.058	1.78
P-I10-S25		1.78	80.2	84.5	1.076	1.80
P-I10-S30		2.14	78.4	82.3	1.067	1.89
P-I10-S40		2.85	80.0	84.6	1.066	1.83
P-I10-S50		3.56	79.8	84.2	1.062	1.84

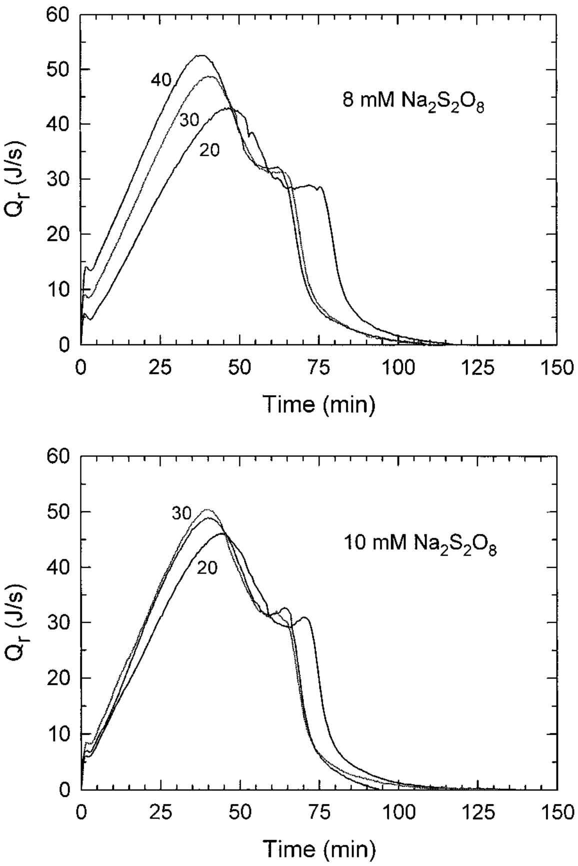

Figure 8. Heat of reaction vs time for the emulsion polymerization of styrene using poly(TREM) as surfactant at 8 mM [$Na_2S_2O_8$], 20, 30, and 40 mM [E] (top) and 10 mM [$Na_2S_2O_8$] and 20, 25, and 30 mM [E] (bottom). T_r = 60 °C.

increasing ionic strength (initiator plus stabilizer) more aggregation can occur. So any increase in particle number might be offset by increased aggregation. The particle sizes of these latexes were also measured by TEM, and the results are consistent with the results obtained by CHDF. The polydispersity index (PDI) data presented in Table 5 show that the latexes prepared with poly(TREM) had narrower particle size distributions than the corresponding latexes prepared using TREM LF-40 (Table 2). This could be related to the differences in the particle nucleation mechanisms between these polymerizations. When homogeneous nucleation was dominant, the particle size distributions were narrower. The dependencies of R_p (maximum) and N_p on the poly(TREM) surfactant concentration and the average numbers of radicals per particle ($\bar{n}$) are summarized in Table 6. These results indicate that there was a one-to-one correspondence between the rate of polymerization and the number of particles produced, unlike the previous findings with TREM LF-40 as the surfactant. In addition, the dependencies are a function of the initiator concentration, decreasing with increasing $Na_2S_2O_8$ concentration over the same range of poly(TREM) concentrations. This phenomenon is not commonly reported in emulsion polymerizations. Although not understood, it is considered likely that the extensive homogeneous nucleation that is considered to occur in this system is affected by the increased ionic strength as the amount of either initiator or poly(TREM) is increased. Limited particle aggregation is expected to play an increasingly significant role in these reactions with variations in these parameters, resulting in fewer particles. The "brief" constant reaction rate period at the beginning of the polymerization may also be a consequence of this. Previously, Urquiola reported that the particle size increased with increasing initiator concentration for the emulsion polymerization of vinyl acetate using TREM LF-40, a clear indication that extensive limited aggregation had occurred in that system.[15]

Table 6. Dependencies Obtained from Kinetics of Emulsion Polymerization of Styrene at 60 °C Using Poly(TREM)

[$Na_2S_2O_8$] (mM)	[poly-(TREM)] (mM)	$Q_r(R_p) \propto [E]^A$ A	$N_p \propto [E]^B$ B (by CHDF)	$Q_r(R_p) \propto N_p^C$ C
5	20−50	0.47	0.47	1.02
8	20−40	0.28	0.28	1.04
10	20−30	0.25	0.24	1.00

[$Na_2S_2O_8$] (mM)	$\bar{n}$ at $R_{p,max}$ [E] = 1.43 mM	[E] = 2.14 mM	[E] = 2.85 mM
5	0.315	0.312	0.314
8	0.310	0.314	0.311
10	0.312	0.309	0.314

Another unusual phenomenon seen in the emulsion polymerization of styrene using poly(TREM) was that the reaction rate and number of particles became nearly independent of the stabilizer concentration at an initiator concentration of 10 mM. Again, one possible explanation lies in the effect that the ionic strength has on the emulsion polymerization. With increasing poly(TREM), the ionic strength increases. An increase in the number of particles generated might be offset by increased limited aggregation. Another possible reason is that the nucleation period was much longer with poly(TREM) compared to TREM LF-40, and homogeneous nucleation was dominant. This could lead to the nondependence of R_p and N_p on [E] at high [E] and [I]. To gain a better understanding of the causes of these unexpected phenomena is the main purpose of the next step of the work.

Once again, by rearranging the kinetic data, the effects of the initiator concentration on the emulsion polymerization of styrene using poly(TREM) as surfactant can be seen. The heat of reaction vs time curves are given in Figure 9. The corresponding particle size data were previously reported in Table 5. With increasing initiator concentration, the reaction rate generally increased, as did the number of particles. However, this system was not as well-behaved as the TREM LF-40 system; the data are more scattered. The dependencies of R_p and N_p on the initiator concentration are given in Table 7. The results indicate a one-to-one correspondence between R_p and N_p at each poly(TREM) concentration. The dependencies on the initiator concentration were higher than in the case of TREM LF-40 and decreased significantly with increasing surfactant concentration.

c. Comparison of Emulsion Polymerizations Using TREM LF-40 and Poly(TREM). The kinetics of the emulsion polymerization of styrene using the reactive surfactant TREM LF-40, and its polymeric version, poly(TREM), are compared in Figure 10. In each plot, the experiments were conducted under the same conditions except for the surfactant type (i.e., same amounts by weight). It was expected that reaction rates would be faster using TREM LF-40 than poly(TREM) due to

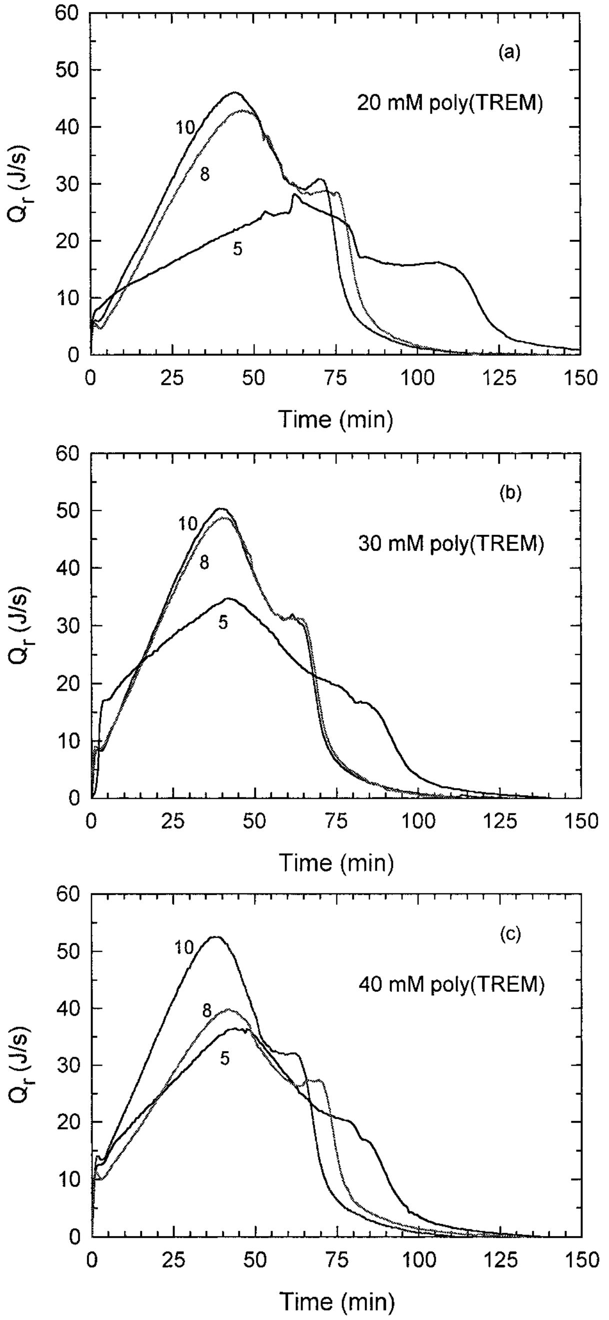

Figure 9. Heat of reaction vs time for the emulsion polymerization of styrene using poly(TREM) as surfactant at (a) 20, (b) 30, and (c) 40 mM and varying [$Na_2S_2O_8$]. T_r = 60 °C

Table 7. Dependencies Obtained from the Kinetics of Emulsion Polymerization of Styrene Using Poly(TREM) as Surfactant

[poly-(TREM)] (mM)	[$Na_2S_2O_8$] (mM)	$Q_r(R_p) \propto [I]^A$ *A*	$N_p \propto [I]^B$ *B*	$Q_r(R_p) \propto N_p^C$ *C*
20	5−10	0.73	0.71	0.99
30		0.56	0.56	1.00
40		0.40	0.44	1.10

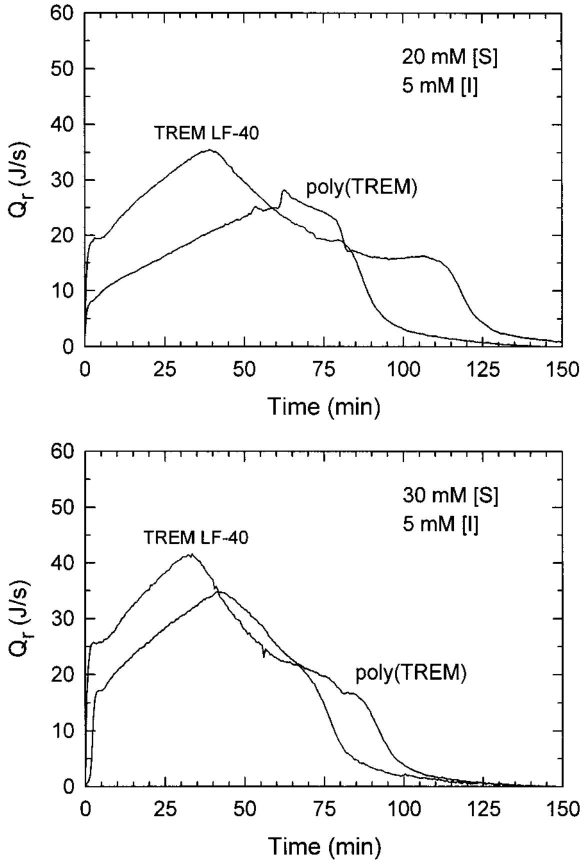

Figure 10. Comparison of the kinetics of emulsion polymerization of styrene using TREM LF-40 and poly(TREM) (based on the monomeric TREM LF-40 molecular weight) as the surfactants at [E] = 20 mM (top) and 30 mM (bottom), [$Na_2S_2O_8$] = 5 mM. T_r = 60 °C.

the differences in the numbers of micelles and the particle nucleation mechanisms. This is seen in the initial fast rise in the rate (interval I), which ends at a higher rate for the TREM LF-40 reactions. On the basis of the proposed mechanism, the relative extent of homogeneous nucleation to micellar nucleation is greatest in the poly(TREM) reactions (ratio of the increase in rate in stage 2 to interval I). The assumption here is that the number of particles formed is proportional to the rise in rate. This has yet to be proven precisely experimentally. The polymeric surfactant produced fewer particles compared to the small molecule (monomeric) surfactant due to the fact that more poly(TREM) was adsorbed per unit area of particle surface. The consequence of this can be seen in the following analysis.

The estimated surface area of the particles (from D_v) is graphed in Figure 11 as a function of the saturation area for the two surfactants. The latter was calculated assuming that all of the surfactant is present on the surface, and it occupies the same surface area per molecule (a_s) as reported earlier. Four sets of data are represented by the two surfactants, TREM LF-40 and poly(TREM), at two initiator concentrations. Linear regressions were performed only on the data obtained for TREM LF-40, and the slopes are reported on the graph. It was not expected that the data for poly(TREM) would correlate with those for TREM LF-40 considering the considerable differences between the two stabilizers. Despite these differences, the results for poly(TREM) do correlate surprisingly well with those of the reactive surfactant, indicating that the resulting surface areas (or particle size and number) are largely influenced by the capacity of the surfactant, whether reactive or polymeric, to stabilize a given area based on their adsorption areas. These results also imply that these areas are largely established prior to the reaction of the surfactant (either as homopolymer, copolymer, or grafted polymer). If this were not the case, the adsorption areas

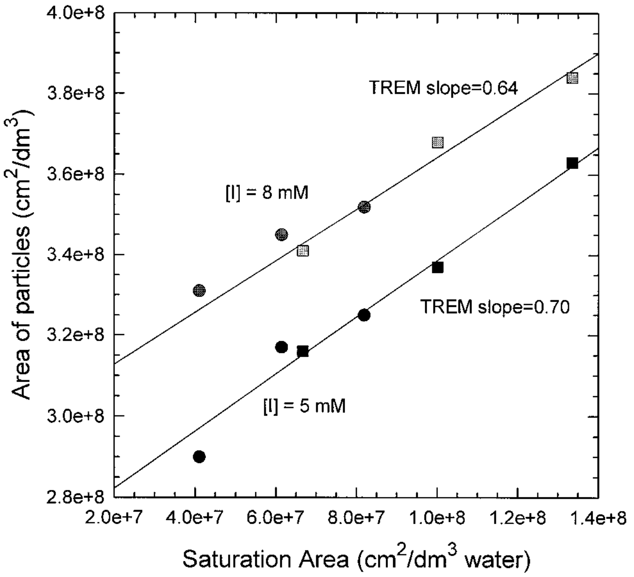

Figure 11. Particle surface area vs saturation surface area of the surfactants at two levels of initiator: TREM LF-40 (■) and poly(TREM) (●).

per molecule applied in these estimations would not be correct. The homopolymerization and copolymerization of the surfactant would create surface active species with differing adsorption characteristics. The correlation between TREM LF-40 and poly(TREM) then should not exist as found in Figure 11.

Conclusions

The emulsion polymerization of styrene using the reactive surfactant, TREM LF-40, and its polymeric counterpart, poly(TREM), was studied. The two surfactants were characterized to determine their cmc's and adsorption isotherms. The cmc's were 1.4 and 0.33 mM for TREM LF-40 and poly(TREM), respectively. The adsorption studies determined values of a_s to be 55.4 and 478 Å^2/molecule, respectively.

The polymerization kinetics showed that the dependencies of R_p and N_p on the TREM LF-40 concentration were not equal. The use of TREM LF-40 gave $R_p \propto [E]^{0.3-0.4}$ and $N_p \propto [E]^{0.5-0.6}$. However, these dependencies were equal for poly(TREM) ($R_p \propto [E]^{0.3-0.5}$ and $N_p \propto [E]^{0.3-0.5}$). The latter dependence on [E] was lower than the classical Smith–Ewart case (0.6) for styrene, and it also decreased with increasing initiator concentration, which was attributed to particle aggregation occurring with increasing ionic strength. Nucleation was divided between micellar and homogeneous nucleation, the latter being more significant when using poly(TREM).

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