Kinetics of Particle Growth in Emulsion Polymerization Systems with Surface-Active Initiators

Joseph M. H. Kusters,[†] Donald H. Napper, and Robert G. Gilbert[*]

School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia

Anton L. German

Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

Received March 3, 1992; Revised Manuscript Received August 19, 1992

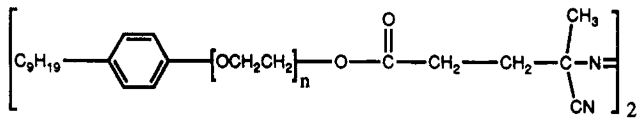
ABSTRACT: The seeded kinetics of particle growth in an emulsion polymerization of styrene where initiation is by a surface-active initiator ("insurf") were investigated. These systems are characterised by a low $\bar{n}$ (average number of radicals per latex particle). The rate coefficient for free-radical exit was obtained using γ-radiolysis relaxation by replacing the inisurf with its (noninitating) surfactant moiety. The resulting value was then used to determine the rate coefficient for radical entry and the initiator efficiency in seeded studies initiated by an inisurf, with varying amounts of surface coverage. The initiator efficiency, calculated using these entry rate coefficients and the measured initiator decomposition rate coefficient, was very low (ca. 0.04%) and independent of surface coverage. This result is readily explained qualitatively and quantitatively by comparison of the time for geminate recombination of the two free radicals formed by inisurf decomposition with the time for escape by diffusion of one of those free radicals from the vicinity of the particle.

Introduction

The preparation of an emulsion polymer always involves surfactant, either added or formed in situ (from the initiator). However, the presence of surfactant can engender certain technical problems. For example, in the application of water-based paints, the surfactant can migrate through the sheet or film of the dried latex, and will concentrate preferentially at the substrate/film or film/air interface. Such surfactant agglomerates can result in low water resistance and subsequent poor aging properties, as well as causing visible imperfections such as "cold blooming" and "blushing".

One solution to these problems is to attach the surfactant chemically to the polymer particles; this can inter alia be achieved by using a polymerizable surfactant. However, this can in turn engender new problems arising from the copolymerization, e.g., unfavorable reactivity ratios. Another way of solving this problem is to make use of a surface-active initiator, or "inisurf",[1-4] designed so that one or both of the free radicals resulting from its thermal decomposition are surface active.

Previous work has concentrated on the synthesis and application of inisurfs in ab initio emulsion polymerization systems (i.e., in the absence of preformed latex particles). However, in developing applications and understanding the formation of polymer colloids made with inisurfs, it is essential to have qualitative and quantitative mechanistic knowledge of the events governing particle formation and growth. It is now accepted[5,6] that such understanding must start with studies of polymer growth in seeded systems: i.e., in the presence of preexisting latex particles and without secondary particle formation. One can then investigate particle growth without the complexities of concomitant particle formation. The knowledge so obtained could be used subsequently to unravel the complexities of particle formation.[7-9] The study presented in this paper deals with the effects of inisurfs on seeded styrene emulsion polymerization, since the growth kinetics of styrene systems with conventional initiators and surfactants are now comparatively well understood. The inisurf employed (structure I) is the diester of 4,4′-azobis(4-cyanopentanoic acid) (the initiator moiety) with poly(ethylene oxide) nonylphenol (the surfactant moiety).



I

With a surface-active initiator, it is expected that the events leading to initiation of propagation inside a latex particle (i.e., entry) would be quite different from those in a corresponding system with a conventional aqueous-phase initiator such as $S_2O_8^{2-}$. In the latter case, it has been established[10] that the mechanism for entry is (1) aqueous-phase propagation of initiator-derived entities to a critical degree of polymerization z, to form a surface-active species $M_zSO_4^{\bullet-}$ (where M = a monomer unit), (2) entry of this $M_zSO_4^{\bullet-}$ into the latex particle that is so fast as not to be rate-determining (in the absence of formation of new particles), and (3) termination among all species in the aqueous phase. In an inisurf system, one might expect instead that the free radicals would be formed at the particle/water interface, and hence that the rate-determining steps for the successful penetration of a free radical into the interior of the particle would be quite different. One would also expect that the presence of polymeric surfactant on the surface of the particle could affect the rate of desorption (exit) of free radicals from the particles in an inisurf-initiated system. It is such questions that we wish to address in the mechanistic studies of the present paper.

The objective of this study is the mechanism of particle growth of a well-characterized polymer latex initiated by inisurf. The questions which might be answered by a study are as follows: What is the initiator efficiency? What is the mechanism for the successful entry of free radicals into the interior of the latex particles? How large is the

---

[*] Author for correspondence and proofs.

[†] Permanent address: Laboratory of Polymer Chemistry, Eindhoven University of Technology.

0024-9297/92/2225-7043$03.00/0

contribution of exit (desorption) of free radicals from the particles, and if significant, what is the mechanism for this loss of free radical activity? What is $\bar{n}$, the average number of free radicals per particle? And, directly following from this point, (a) is termination within the latex particles by entry of a new free radical causing instantaneous termination with another free radical (i.e., does one have a zero–one,[5,6,11] or Smith–Ewart cases 1 and 2 combined,[12] system, with $\bar{n} \leq 0.5$), or (b) is there kinetically significant termination between two growing chains in the particle (in which case $\bar{n}$ may exceed 0.5)?

In the past, the questions, in each point listed above, have been investigated and answered for styrene emulsion polymerizations employing, as experimental data, kinetics in the form of conversion as a function of time. In each case, these kinetic studies have been done on seeded systems in the absence of formation of new particles. The initiator efficiency was investigated by measuring the dependence of the rate coefficient for entry of free radicals into particles on quantities such as initiator concentration[11] and surfactant coverage.[13] Such studies in turn have led to a widely applicable model for the entry process.[10] Exit has been investigated from studies of the time dependence of the approach to steady state both with chemical initiator[11] and with initiation by γ-radiolysis,[14,15] including dependence on particle size, etc.; the resulting data have all been consistent with the transfer-diffusion mechanism[16,17] for exit. Appropriate studies[5,6] of the steady-state polymerization rate have led to a knowledge of the values of $\bar{n}$ in various systems, with concomitant understanding of termination. In addition to these studies of styrene systems, the methodology has also been applied to a number of other monomers.[5]

When this methodology is applied to investigate inisurf mechanisms, certain modifications must be introduced. In a conventional chemically initiated emulsion polymerization, mechanistic information can be gained from studies wherein initiator concentration is varied; in an inisurf-initiated system, the equivalent is to vary the surface coverage of the inisurf. The latex prepared from an inisurf has the surfactant moieties already bonded to the surface. Therefore we choose in the present studies a seed latex prepared from a chemical initiator in a way that most (presumably ionic) surfactant arising from the seed-making process can be subsequently stripped from the surface. The surface coverage can then be changed by adding various amounts of inisurf.

As stated, one of the important techniques used to understand particle growth with conventional initiators is through relaxation studies using γ-radiolysis initiation, whereby polymerization is initiated with γ-rays and the polymerization vessel removed from the ^{60}Co source. This leads to essentially instantaneous loss of aqueous-phase free radicals, and the subsequent relaxation of the polymerization can be used to infer information about radical loss events (exit and termination), which can thus be separated from macroradical creation (entry) events.

Experimental Section

All kinetics were carried out at 323 K, at which temperature there is extensive quantitative knowledge of styrene emulsion polymerization kinetics.

Synthesis of the Inisurf. The inisurf used in these studies was synthesized by the esterification of 4,4′-azobis(4-cyanopentanoic acid) (Fluka AG) with poly(ethylene oxide) nonylphenol (Teric N30, ICI; mean degree of polymerization $n = 30$). Details of the synthesis are described elsewhere,[18] as are the results of unseeded (ab initio) studies with this inisurf.

Seed. The objective of using a seed which can be purged of almost all of the oligomers and other surface-active species formed during its preparation, prior to adding varying amounts of inisurf, required an exceptionally colloidally stable seed which could be cleaned thoroughly, and which could then be swollen with monomer. The seed was also required to be monodisperse. Moreover, since the mechanistic analysis is simplest if the system has $\bar{n} \leq 0.5$, this seed should have a radius of less than 70 nm; it has been established that this results in $\bar{n} \leq 0.5$ over a large range of conditions.[11,19] These requirements were achieved[20,21] by including a comonomer (potassium *p*-styrenesulfonate) in the seed recipe: the comonomer has the effect of increasing the surface charge density of chemically bound charges, on the surfaces of the seed particles. The seed preparation was carried out in a bottle polymerizer at 358 K, agitated by end-over-end rotation at 40 rpm. The recipe consisted of 29.3 g of styrene, 150 g of water, 0.046 mol dm^{-3} potassium *p*-styrenesulfonate, and 0.011 mol dm^{-3} potassium peroxodisulfate.

Cleaning of the Seed. After preparation, the seed latex was cleaned by dialysis against distilled water for 1 week with twice-daily water changes. Any remaining surfactant (which would have been generated from the styrenesulfonate) and excess electrolyte were then more rigorously removed by the ion-exchange method of Kamel.[22] Ion exchange was carried out in a mixed bed of anionic and cationic resins. The resins which were used for cleaning the polystyrene seed latex were 50–100 mesh Dowex 50W (×4), which is a sodium salt of sulfonated 96:4 styrene–divinylbenzene copolymer (4% cross-linking), and Dowex 1 (×4), which is a trimethylammonium methylene derivative of a 96:4 styrene–divinylbenzene copolymer (4% cross-linking). These resins were intensively conditioned before applying them to clean the seed latex, using the method of Vanderhoff and van den Hul,[23] which involved cleaning with solutions of sodium hydroxide and solutions of hydrochloric acid, with methanol, and with hot and cold water in repetitive cycles. The Dowex 50W resin was stored in the H$^+$ form, while the Dowex 1 resin was stored in Cl$^-$ form and converted to the OH$^-$ form shortly before use, by adding an excess of 3 mol dm^{-3} sodium hydroxide. The purity of the resins was determined by measuring the conductivity of the wash water. A conductivity of twice or less than that of distilled-deionized water was tolerated.

For cleaning the latex, the two resins were separately suspended in water and mixed together (in the ratio of 51:49 w/w Dowex 50W:Dowex 1). The water was filtered, and the mixed resins were ready for use. Some of the mixed ion-exchange resins were then added to a diluted latex (ca. 5% solid content) so that the ratio of solid polymer to resins was 1:1 by weight. This mixture was agitated for 2 h. To remove the resin beads afterward, the mixture was filtered through glass wool. The ion-exchange procedure was repeated until the conductance of the latex did not differ notably between subsequent cycles. This took four ion-exchange cycles. The solids content of the resulting latex was 3.12%.

The latex was sized by calibrated transmission electron microscopy; the radius was found to be 37.2 nm with a standard deviation of 2.8 nm.

Experimental Technique for Determining Seeded Polymerization Kinetics. Kinetic data, in the form of fractional conversion as a function of time, were obtained by automated dilatometry. To avoid problems with secondary nucleation, the amount of monomer added to the cleaned seed was such that all runs were commenced at the lowest weight fraction of polymer that still maintained the system in Interval III (absence of monomer droplets). This also ensured that the only phase onto which inisurf could be adsorbed with the polymer latex. Since the initiating moiety of the inisurf is an azo initiator, nitrogen is formed during its dissociation. The formation of gas bubbles in the dilatometer thus had to be avoided. This was accomplished by keeping the concentration of inisurf in the dilatometer at 3.2×10^{-4} mol dm^{-3} (this is below the solubility concentration of nitrogen in water at 323 K) and by thoroughly degassing the water before use. In all the runs the inisurf concentration was kept at the highest possible concentration within this constraint. Variation in coverage of the seed particle with inisurf was then

Table I
Recipes and Steady-State $\bar{n}$ Values for Seeded Runs

	amt of seed (g)	amt of monomer (g)	amt of insurf (g)	amt of water (g)	coverage (%)	N_I[a]	steady-state $\bar{n}$
1	72.43	4.04	0.06	26.64	7	0.9×10^3	0.03
2	31.02	1.80	0.11	70.84	21	3.0×10^3	0.06
3	20.38	1.13	0.11	82.18	28	3.9×10^3	0.16
4	15.21	0.93	0.11	87.37	32	4.7×10^3	0.17
5	10.35	0.57	0.11	91.98	40	5.6×10^3	0.16
6	10.37	0.55	0.11	92.85	40	5.6×10^3	0.26
7	7.76	0.49	0.11	94.67	45	6.7×10^3	0.22

[a] N_I = number of inisurf molecules per latex particle. Weight-average molecular weight of inisurf = 3330. Area per inisurf molecule = 2.64 nm^2.

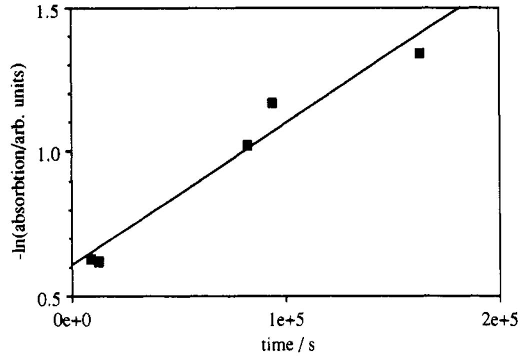


Figure 1. Optical absorption as function of time for decomposition of inisurf.

achieved by using different amounts of seed latex. Recipes used in various runs are given in Table I.

The procedure for kinetic runs was a follows. The appropriate amount of seed latex was charged into the dilatometer and the corresponding amount of monomer added. The mixture contained in the dilatometer was emulsified in an ultrasonic bath for some minutes and left overnight with slow agitation. A solution of inisurf in thoroughly degassed triply distilled water was added to the dilatometer. Thoroughly degassed triply distilled water was then added to the dilatometer vessel to reach the required volume. Conversion as a function of time was measured by automated dilatometry. The absence of secondary nucleation was confirmed by transmission electron microscopy for all runs.

Measurement of Dissociation Rate Coefficient of the Inisurf. The first-order dissociation rate coefficient k_d was obtained from UV measurements of inisurf solutions at 323 K, using the method of Blackley and Haynes.[24] The azo bond absorbs at 370 nm, and hence decomposition was followed by measuring the optical density of the solutions at 370 nm using cells having a path length of 10 mm. The optical densities were converted to concentration by means of a calibration curve obtained from the measured optical density of the benzene ring of the surfactant moiety for a range of solutions of known concentration. The resulting value of k_d was found to be 5×10^{-6} s^{-1}. This is of a similar magnitude to values of k_d of 1.6×10^{-6} s^{-1} [25] for AIBN and of 1.8×10^{-6} [24] and 1×10^{-6} s^{-1} [26] for 4,4′-azobis(4-cyanopentanoic acid) (the acid part of our inisurf). The measured absorption intensities are plotted as − ln (absorption) versus time in Figure 1. The value of k_d was calculated from these results.

It might be argued that the location and configuration of the inisurf on the surface of the latex particle, being rather different from those in the medium in which the foregoing measurements were carried out, might effect the value of k_d significantly. Some information pertaining to this can be gleaned from investigations of solvent effects on this quantity. A number of such studies[24,26-28] show that solvent effects are relatively small. It is therefore felt that any such environmental effects for an inisurf will be sufficiently small so as not to change qualitatively what will emerge as an important result of the present study: the minuscule initiator efficiency.

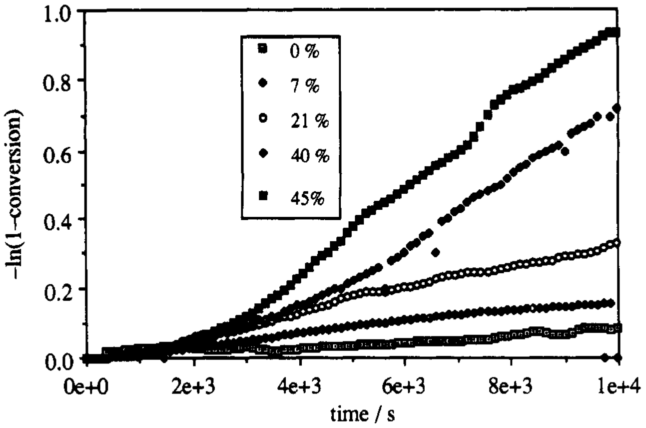


Figure 2. − ln (1 − x) versus time for inisurf-initiated systems with different percentages of surface coverage of the monomer-swollen polymer particles.

Results

In an emulsion polymerization, the time evolution of fractional conversion x is given by

$$\frac{dx}{dt} = \frac{k_p C_M N_c}{n_M{}^0 N_A} \bar{n} \qquad (1)$$

where k_p is the propagation rate coefficient, C_M is the monomer concentration in the latex particles, N_c is the particle concentration, $n_M{}^0$ is the initial number of moles of monomer per unit volume of reaction medium, and N_A is Avogadro's constant. Since in the absence of separate monomer droplets and low water solubility of the monomer, one has $C_M = C_M{}^0(1 - x)$, where $C_M{}^0$ is the initial monomer concentration in the latex particles, eq 1 can be rewritten for Interval III conditions as

$$-\frac{d \ln (1 - x)}{dt} = \frac{k_p C_M{}^0 N_c}{n_M{}^0 N_A} \bar{n} \equiv A\bar{n} \qquad (2)$$

This suggests that the optimal means of displaying Interval III kinetic data is as a plot of − ln (1 − x) against t. Some of the data, for varying amounts of surface coverage by inisurf, are plotted in Figure 2. These data show a steady-state region (the small fluctuations in rate in the steady-state region seen by close inspection of Figure 2 are typical for data from the equipment used and arise from small but regular temperature variations arising from the thermostat in the course of the run and from "jitter" inherent in the tracker of the automated dilatometer). Numerical differentiation of the data of Figure 2 gives the steady-state values of $\bar{n}$ displayed in Table I, calculated using $k_p = 258$ dm^3 mol^{-1} s^{-1}.[11] The steady-state $\bar{n}$ values show that the system is indeed in the zero–one regime, as expected.

The data of Figure 2 also show an apparent approach to steady state. If this approach to steady state is not some artifact due to inhibition effects and the starting time for the reaction is precisely known, then these data could be used to infer the rate coefficients for entry and exit in these zero–one systems.[5,6,11] A check for the presence of inhibition effects was carried out using the following method.[11,29] The aqueous-phase free radicals produced by γ-radiolysis are able to completely "burn out" inhibitors in a short time, and hence a suitable test for inhibition effects is to carry out a kinetic run under radiolysis, observe the rate of approach to steady state on the first insertion into the ^{60}Co source, remove from the source and let the system relax to its background thermal rate, and then reinsert into the source and observe the

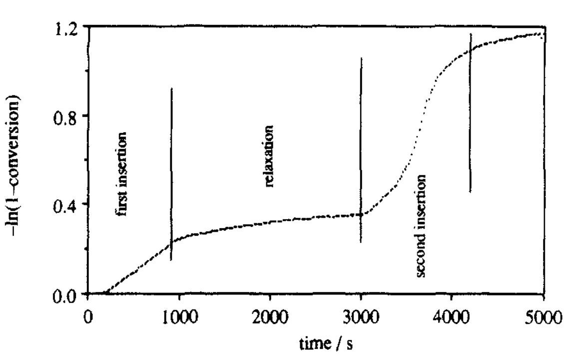


Figure 3. $-\ln(1-x)$ versus time for γ-initiated systems at first insertion, relaxation, and second insertion, for systems stabilized with the surfactant moiety of the inisurf.

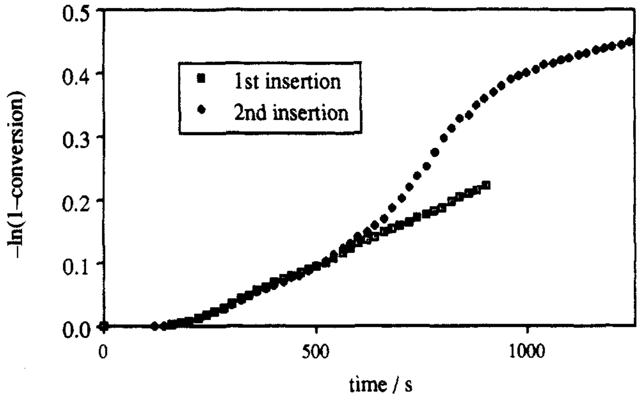


Figure 4. Data for first and second insertions of Figure 3, superimposed to show that these exhibit the same kinetics for approach to steady state.

rate of approach to steady state after this second insertion. If the rates of approach to steady state in the first and second insertion are the same, then inhibitor-induced artifacts are absent. This was implemented by using a seed 29% covered with the nonionic surfactant moiety of the inisurf instead of the inisurf itself. This coverage was calculated from literature data[30] for the absorption area and adsorption isotherm of poly(ethylene oxide) nonylphenol on polystyrene latex particles. In these calculations, both the area and the absorption isotherm of poly(ethylene oxide) nonylphenol were taken into account. The area of one inisurf molecule was presumed to be twice that of one surfactant molecule since one inisurf molecule consists of two surfactant moieties. The assumption made here is that the nonionic surfactant behaves similarly to the inisurf, as far as the kinetics of inhibition are concerned. In confirmation of this, it was found that the approach to steady state from the second insertion was about the same as that from the first, as shown in Figure 3 and 4.

Given this result that the inisurf behaves as an inhibitor and not a retarder, it is tempting to then use the observed rate of approach to steady state in systems where only inisurf is used for initiation to obtain values for the entry and exit rate coefficients.[5] However, in the present case such a treatment is not possible. This is because the method of preparation of the system, including adsorption of the inisurf onto the seed particles, is such that it is impossible to identify accurately the starting time for the polymerization, since the reaction commences while the system is still undergoing thermal equilibration.

While this shows that the approach to steady state seen with inisurf initiation cannot be used to infer kinetic information, the steady-state rate itself can, because it is reasonable to assume that inhibitor has been completely removed when the system attains its steady state. The steady-state value of $\bar{n}$ in these zero–one systems is then given by[6,11]

$$\bar{n}_{\mathrm{SS}} = \frac{\rho}{2\rho + k} \tag{3}$$

where ρ is the first-order rate coefficient for entry of free radicals into the interior of the particles (where they can propagate at the "bulk" rate) and k is the first-order rate coefficient for free-radical loss from the particles. Hence if a value of k is available from another experiment, the value of ρ can be inferred from the experimental $\bar{n}_{\mathrm{SS}}$.

A value of k can be determined from γ-radiolysis relaxation experiments,[6,14] as mentioned above, by watching the rate of relaxation after removal from the source (when all inhibitor will have been scavenged by the radiolysis process). A complication in applying this to an inisurf system is that, because the inisurf functions as both stabilizer and initiator, upon insertion into the source it is likely that $\bar{n}$ will exceed 0.5, i.e., that termination must be taken into account in interpreting the kinetics. Termination kinetics have been shown to be quite complex because of the chain-length dependence of k_t,[31-33] and it would be very hard to produce an unambiguous interpretation of the kinetics in a system in which both termination and exit were significant radical-loss events. Because of this, we adopted the approach of finding k by the γ-radiolysis relaxation technique for a latex covered only with the surfactant moiety of our inisurf. The absence of any source of free radicals except γ-rays of sufficiently low intensity ensures that the system is truly zero–one. The value of k so obtained can then be used for our inisurf system, by assuming that the exit kinetics are unaffected by the absence of the initiating moiety of the inisurf.

Results of the relaxation experiment are shown in Figure 3. Treating these data using the "slope–intercept" method as described elsewhere[6] with the assumption (found to be appropriate to γ-relaxation experiments in normal emulsion polymerization systems[34]) that all desorbed free radicals will reenter the particles (i.e., assuming that the dimensionless "fate parameter" which takes account of the aqueous-phase kinetics of desorbed free radicals[6] takes the value $\alpha = +1$) yields $k = 5.6 \times 10^{-4}\ \mathrm{s}^{-1}$. The corresponding value of the rate coefficient for background or thermal entry of free radicals[6] was $\rho_{\mathrm{therm}} = 3 \times 10^{-6}\ \mathrm{s}^{-1}$. Now, for systems such as these where there is a layer of polymeric surfactant around the latex particle, it might be argued that desorbed free radicals (in the condition of absence of aqueous phase free radicals as pertaining to γ-radiolysis relaxation) could well homoterminate in the aqueous phase instead of (or in competition with) reentering. This is equivalent to assuming that $\alpha = 0$; interpreting the relaxation data of Figure 3 with this alternative assumption yields $k = 7.4 \times 10^{-5}\ \mathrm{s}^{-1}$ and $\rho_{\mathrm{therm}} = 4 \times 10^{-6}\ \mathrm{s}^{-1}$. These values may be compared with those found at 323 K, for normal emulsion polymerizations, from the data of Hawkett et al.[11] and Morrison et al.,[7] viz., $k\ (\mathrm{s}^{-1}) = 4.3/(r_{\mathrm{S}})^2$, where r_{S} is the swollen radius in nm. The values for k found in the present system are found to be 1 order of magnitude smaller than that for latex particles in conventional emulsion polymerizations of the same size. This could be explained if the polymeric surfactant were to decrease the rate of exit. This in turn can be rationalized as follows, in terms of the transfer-diffusion mechanism for exit,[16,17] for which there is now a considerable body of supporting evidence.[5,7,35] The polymeric surfactant could well form a "hairy" layer near the particle surface which could greatly decrease the rate at which a monomeric free radical can diffuse into the bulk phase, with a comcomitant decrease in the rate of exit.

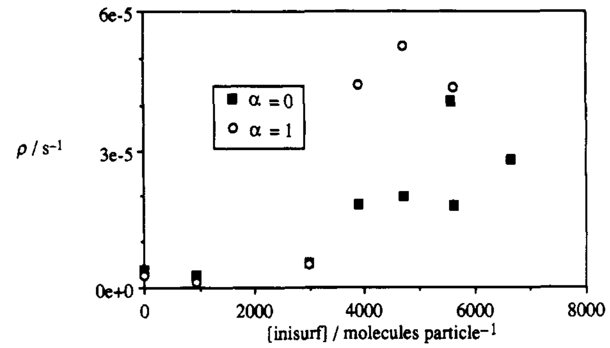


Figure 5. First-order rate coefficient for entry (ρ), for different inisurf surface coverages, deduced from the steady-state with $\alpha = 0$ and $\alpha = 1$.

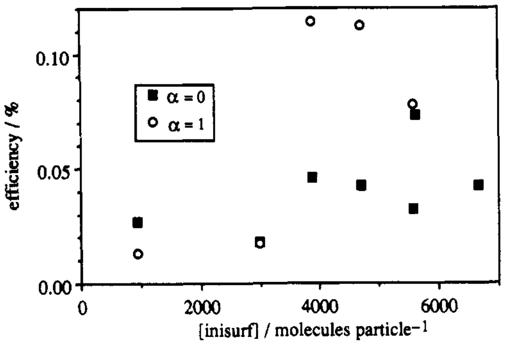


Figure 6. Initiation efficiency of inisurf for different amounts of surface coverage, deduced from values of ρ for $\alpha = 0$ and $\alpha = 1$.

The value of k thus obtained for 29% coverage by the noninitiating analog of the inisurf was assumed to be independent of surface coverage and also to hold for inisurf. While this assumption is certainly not very accurate, it should certainly be sufficient to enable us to estimate ρ from eq 3 to within 1 order of magnitude using the $\bar{n}_{SS}$ from the inisurf-initiated runs of Figure 2. The values of ρ so obtained are displayed in Figure 5. From these, one can calculate the initiator efficiency f as

$$f = \rho / 2k_dN_I \tag{4}$$

where N_I is the number of inisurf molecules per particle. The results are shown in Figure 6. Values of f computed for both $\alpha = 0$ and 1 are of similar magnitude. What is remarkable about these results is that, while ρ increases with coverage as one would expect, the efficiency is only very weakly dependent on coverage, and indeed could be said to be independent of coverage within the uncertainty of the experimental data. Figure 6 shows at most only a slight trend with coverage, with f changing by at most a factor of 2 while the coverage varies by more than a factor of 6.

Discussion

The first point to be considered is the observation that the initiator efficiency for our inisurf is apparently independent of (or perhaps only weakly dependent on) surface coverage. This result can be immediately explained as follows. The value of k_d implies that the rate of decomposition per particle, N_Ik_d, is low: $N_Ik_d = 2.5 \times 10^{-2}$ s^{-1} for $N_I = 5 \times 10^3$ molecules per particle (see Table I), i.e., a typical time of 40 s between inisurf decomposition events in a given particle. A good starting point is to assume that the free radicals which commence propagation inside the latex particles originate from an inisurf decomposition on the surface of the *same* particle (rather than by a free radical which exited from another particle and reenters from the aqueous phase). This hypothesis implies that initiator efficiency must be controlled solely by the dynamics of the two free radicals formed by the decomposition of a single inisurf molecule; i.e., f must by this hypothesis be independent of the amount of inisurf on the surface of a given particle. The results of Figure 6, showing this independence, are thus completely consistent with the original hypothesis, viz., that the free radicals which enter the interior of the particle and cause formation of macroradicals predominantly arise from the decomposition of inisurf molecules on the same particle. The corollary that reentry of exited free radicals is kinetically insignificant can be seen to be consistent with the observation that the exit rate coefficient k in these systems is small, for reasons discussed above. Moveover, these conclusions suggest that the correct values for ρ and f are those obtained assuming $\alpha = 0$, rather than $\alpha = 1$ (the latter implying complete reentry).

The next observation from the data is that the initiator efficiency is extremely low: ca. 10^{-4}. This contrasts with typical efficiencies of 0.1–1 in emulsion polymerization systems with conventional chemical initiators,[5] the explanation for these chemical-initiator efficiencies now being well understood.[10] The very low efficiency with an inisurf can be understood qualitatively and quantitatively by the hypothesis that, because of the close confines of the particle, very rapid geminate recombination will occur between the two free radicals formed by inisurf dissociation *unless* one of them can desorb into the aqueous phase. This hypothesis can be quantified as follows.

Derivation of Expression for Initiator Efficiency. After an inisurf molecule has dissociated, each of the resulting free radicals can undergo one of the following fates: propagation, desorption, or geminate recombination. By our hypothesis, propagation to form a macroradical can only occur if one of the free radicals formed by inisurf decomposition desorbs into the aqueous phase, whereupon its geminate partner is free to propagate within the particle: an entry event (which we emphasize is completely different from entry with a conventional initiator such as persulfate, where the mechanism involves aqueous-phase propagation and termination.[10] Influences such as the likelihood of a more viscous surface layer on the particle in the present system will therefore have no effect on "entry" once one of the geminate free radicals has escaped from the particle). Now, simple time scale arguments show that propagation is much slower than geminate recombination. The time scale for propagation is given by $t_p = 1/(k_p{}^1C_M{}^S)$, where $k_p{}^1$ is the rate coefficient for propagation of the inisurf free radical with a monomer unit (note that this may well be different from the k_p for propagation of a macroradical) and $C_M{}^S$ is the concentration of monomer in the surface layer of the particle. A typical value for $k_p{}^1$ for free radicals resulting from decomposition of initiators of the type in our inisurf is ca. 10^5 dm^3 mol^{-1} s^{-1}.[36] In the present system, a reasonable value to take for C_M is 3.4×10^{-3} mol dm^{-3}, which is the saturated aqueous-phase concentration: the radical is likely to be proximate to the aqueous phase. This yields $t_p \approx 10^{-3}$ s. If instead the calculation is done for the upper bound of C_M of 5 mol dm^{-3} (the saturated polymer-phase concentration), one obtains instead $t_p \approx 10^{-6}$ s. However, the radical formed from inisurf decomposition will be in the surface layer of inisurf around the particle. The thickness of this surface layer is at most the stretched length of the water-soluble part of the surfactant radical. The concentration of monomer in this surface layer will be far less than the concentration of monomer in the polymer particle. For this reason, we presume that the concentration will be close to the saturation concentration of monomer in water, and thus that $t_p \approx 10^{-3}$ s is a better estimate. As shown below, the time scale for termination, t_t, is significantly shorter than this: $t_t \approx 10^{-6}$ s. Hence for the purpose of an order-of-magnitude estimate of the initiator efficiency, the only events we need to consider are desorption and termination. Hence the efficiency f can be written as

$$f = \frac{\text{rate of desorption}}{\text{rate of desorption + rate of geminate recombination}} \tag{5}$$

Moreover, as will be seen when quantitative values are obtained for the rates of geminate recombination and desorption, the latter is orders of magnitude slower than the former, and hence one has to an excellent approximation

$$f = \frac{\text{rate of desorption}}{\text{rate of geminate recombination}} = \frac{k_{de}}{2k_t[R^\bullet]} \tag{6}$$

where k_{de} is the first-order rate coefficient for desorption of a free radical from a particle and k_t the second-order rate coefficient for termination of free radicals within the particles (note that in general k_t depends on the length of each chain;[32,33] however, in the present case, we are considering geminate recombination of two radicals formed by decomposition of a single molecule, and hence this chain-length dependence does not need to be explicitly indicated).

We now give estimates of the quantities required in eq 6. The mechanism of desorption from a latex particle of a monomeric free radical originating from transfer to monomer is well understood.[15-17,37] However, the present case is for desorption of a *surface-active* free radical, and thus the cited theory cannot be employed. However, an expression for the desorption rate coefficient of a surface-active free radical from the surface of a a particle can be readily derived using exactly the same procedure as used to derive that for an ordinary (non-surface-active) monomeric free radical,[16] viz., from the microscopic reversibility relation[38] relating the forward (adsorption) and reverse (desorption) rate coefficients. The final result is[39]

$$k_{de} = k_{ad}\frac{a}{A_S b} \tag{7}$$

where k_{ad} is the rate coefficient for absorption, $A_S = 4\pi r_S^2$ is the surface area of the monomer-swollen particle, and a and b are the Langmuir adsorption isotherm quantities for the partitioning of the surface-active species between the continuous phase and the particle surface: i.e., the quantities in the Langmuir adsorption isotherm expression (e.g., see ref 40)

$$A = a\left(1 + \frac{1}{[S_{aq}]b}\right) \tag{8}$$

where A is the area occupied per surfactant molecule on the particle surface at an aqueous-phase concentration of surfactant, $[S_{aq}]$. The quantity a is thus the close-packed area per surfactant molecule. The adsorption rate coefficient can be obtained from the Smoluchowski equation (there is now experimental evidence[7] that this is quantitatively applicable to adsorption of small species onto latex particles):

$$k_{ad} = 2\pi N_A D_W (r_{st} + r_S) \tag{9}$$

where N_A is Avogadro's constant, D_W is the mutual surfactant/particle diffusion coefficient in the medium (in this case, water), r_{st} is the hydrodynamic radius of the surfactant, and r_S is that of the particle; implicit here is the assumption that the hydrodynamic and swollen radii of the particle are the same. Since $r_{st} \ll r_S$, we have $k_{ad} = 2\pi D_W r_S$. The surfactant/particle mutual diffusion coefficient can be approximated as that of the surfactant, which in turn can be estimated from the Stokes–Einstein relation:

$$D_W = \frac{k_B T}{6\pi\eta_W r_{st}} \tag{10}$$

where η_W is the viscosity of the medium. The final result is

$$k_{de} = \frac{N_A k_B T a}{12\pi r_{st}\eta_W r_S b} \tag{11}$$

An expression for k_t is obtained by noting that this process is diffusion-controlled, and hence the Smoluchowski equation can be employed again. For termination of small species (such as those formed by decomposition of an inisurf) it is often assumed[31] that the diffusion process involved is segmental. However, in the present case, the species are so small (mean number of ethylene oxide units $n = 30$) that center-of-mass diffusion of the whole entity is probably rate-determining. In this case, one then has for this diffusive encounter of two identical species

$$k_t = 4\pi D_S N_A r_{st} \tag{12}$$

where D_S is the diffusion coefficient in the surface layer. Note that it could be argued that the encounter radius for termination should be smaller than the size of the surfactant; however, a more sophisticated description would not change the predictions of eq 12 by more than (say) a factor of 5 for these small entities, and so eq 12 is quite adequate for our present purpose of semiquantitative explanation.

The final step in the evaluation of eq 6 is to estimate $[R^\bullet]$, the concentration of the free radicals formed by decomposition of inisurf. We assume that the radicals are randomly distributed throughout a surface layer of thickness d. Since the number of free radicals is 2, we have

$$[R^\bullet] = \frac{2}{N_A}\frac{1}{(4/3)\pi[(r_S + d)^3 - r_S^3]} \approx \frac{1}{2\pi N_A r_S^2 d} \tag{13}$$

the last step following because $r_S \gg d$. Using the Stokes–Einstein relation, one then has

$$2k_t[R^\bullet] = \frac{2k_B T}{3\pi\eta_S d r_S^2} \tag{14}$$

where η_S is the viscosity in the surface layer. The final result is then

$$f = \frac{N_A d r_S a \eta_S}{8 r_{st} b \eta_W} \approx \frac{N_A d r_S a}{8 r_{st} b} \tag{15}$$

if we ignore any difference between the viscosity of the water and of the surfactant layer. Admittedly, when we make this last approximation, we are aware that the small value of the exit rate coefficient found for this system, and ascribed to slower diffusion in a surface layer, could make the viscosity in the surface layer somewhat greater than that in water; however, this would only change the quantitative but not qualitative substance of the present calculation.

We now turn to an evaluation of the efficiency for the present system. The swollen radius $r_S = 55$ nm. We take

$r_{st} = 0.9$ nm, as calculated with the Le Bas additive volume method.[41] The area a is found by interpolation of the literature data for adsorption of poly(ethylene oxide) nonylphenol[30] and is 1.32 nm^2. The thickness d of the surfactant-containing shell is presumed to be the length of the water-soluble part of the inisurf, in a totally stretched conformation; this gives $d = 6.3$ nm. The adsorption isotherm quantity b can be estimated from studies by Kronberg et al.[30] of the adsorption of poly(ethylene oxide) nonylphenol on polystyrene latex particles (radius: 213 nm) at 298 K. Note that these authors used the same Langmuir adsorption isotherm as in eq 8, albeit expressed in a slightly different way; their equilibrium constant K governing the surfactant partitioning between the continuous and surface phases is related to the quantity b of eq 8 by

$$b = K\frac{M_c}{d_c} \tag{16}$$

where M_c and d_c are respectively the molecular weight and density of the continuous phase (which is water in the present case). These authors reported $K = 2.3 \times 10^6$. The temperature dependence of this quantity is unknown, but use of the data for $T = 298$ for 323 K should not make a significant difference for our purpose of an order-of-magnitude estimate. The same remarks hold for the relatively weak dependence of b on particle size,[42] and to the unknown, but relatively broad, molecular-weight polydispersity of the inisurf, which should not have any effect on the order-of-magnitude estimate which is our present purpose. While the values of the quantities a and b which we use here are for entities somewhat different in configuration and molecular weight distribution to those of our inisurf, the differences between values for surface-active species of the same generic type are never sufficiently large (e.g., see ref 42) as to invalidate the demonstration that order-of-magnitude estimates yield to a value of the initiator efficiency which is consistent with our proposed mechanism.

These quantities then give the final result that $f = 9 \times 10^{-4}$ for the present system. This is indeed the order of magnitude of the value inferred from our experiments (Figure 6), viz., ca. 10^{-4}. While one can certainly quibble about the precise values of the quantities used in this evaluation and the approximations inherent in its derivation, we feel that more precise treatments would not change the order of magnitude of the result. The accord between the calculated and experimental efficiencies thus suggests the correctness of the basic model used in the derivation. In addition, our conclusion that geminate recombination among initiator moieties is highly probable in the confined vicinity of a latex particle is in accord with the finding[43] that initiation with lipophilic initiators such as AIBN occurs more readily via the small number of radicals generated by *aqueous-phase* decomposition, for exactly the same reason.

An important conclusion from this model is that the initiator efficiency should increase with an increase in water solubility of one of the surface-active moieties of the inisurf. Synthesis and applications of this inisurf will be presented in a future publication.

Lastly, we note that the exit rate coefficient is low in these inisurf systems, but also the entry rate coefficient (or equivalently the initiator efficiency) is even lower. Hence one would expect that zero–one conditions (which were obtained by design in the present studies) could be attained over a range of conditions wider than normal in emulsion polymerizations. Precise prediction of the requisite conditions could be carried out using standard means,[6] given the quantitative knowledge of initiator efficiency and exit deduced in this paper. For an inisurf system, the rate coefficient for entry, ρ, can be calculated from eq 4 and 15.

Conclusion

Initiating surfactants (inisurfs) have considerable potential for the production of specialty polymer colloids through emulsion polymerizations, by enabling one to grow a latex where the surfactant is chemically bonded to the polymer which comprises the latex particle. The present study has examined (using the technique of γ-radiolysis relaxation and steady-state rate) the kinetics of seeded particle growth with these entities to infer the mechanism of exit and the factors controlling initiator efficiency. The rate coefficient for exit is found to be lower than in a corresponding ordinary emulsion polymerization system, a result which can be readily rationalized (in terms of the generally accepted transfer-diffusion model for exit) by noting that the desorbing free radical must diffuse through a layer of polymeric surfactant (the inisurf or its decomposition product), and hence the rate of diffusion away from the particle of an exiting free radical must be slower than in a conventional emulsion polymerization where ionic stabilizers are employed. The efficiency of initiation by an inisurf is found to be extremely low: orders of magnitude less than in a conventional emulsion polymerization with a water-soluble initiator. This result is explained quantitatively by assuming that the decomposition products of an inisurf will undergo geminate recombination very quickly on the surface of the latex particle (resulting in no polymer formation) unless one moiety is able to desorb. Although these studies do not directly indicate how to solve certain technical problems arising from the use of surfactants in latexes prepared for surface coatings (for example, they indicate that very little of the original inisurf will be chemically bonded to polymer in the latex particle), the mechanistic understanding gained from these studies can be used to improve the design and choice of initiating surfactant.

Acknowledgments. We gratefully acknowledge the Australian Government, Department of Employment, Education, and Training, for financial support under the Australian-European Awards Program. Support by the Australian Research Grants Committee and by the Australian Nuclear Science and Technology Organization are gratefully acknowledged, as is the Sydney University Electron Microscope Unit for generous provision of facilities. Advice and help from Mr. David Sangster were of great benefit to this work. The assistance of Mr. Phillip Moffatt in measuring the dissociation rate coefficient of the inisurf is especially appreciated.

References and Notes

(1) Ivanchev, S. S.; Pavljuchenko, V. N. *Acta Polym.* **1981**, *32*, 407.
(2) Ivanchev, S. S.; Pavljuchenko, V. N.; Byrdina, N. A. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 47.
(3) Tauer, K.; Goebel, K.-H.; Kosmella, S.; Neelsen, J.; Stähler, K. *Plaste Kautsch.* **1988**, *35*, 373.
(4) Tauer, K.; Goebel, K.-H.; Kosmella, S. *Makromol. Chem., Macromol. Symp.* **1990**, *31*, 107.
(5) Napper, D. H.; Gilbert, R. G. In *Comprehensive Polymer Science*; Allen, G. A., Bevington, J. C., Eastwood, G. C., Eds.; Pergamon: Oxford, U.K., 1989; Vol. 4, p 171.
(6) Gilbert, R. G.; Napper, D. H. *J. Macromol. Sci., Rev. Macromol. Chem. Phys. C* **1983**, *23*, 127.
(7) Morrison, B. R.; Maxwell, I. A.; Gilbert, R. G.; Napper, D. H. In *Polymer Latexes—Preparation, Characterization and Applications*; Daniels, E. S., Sudol, E. D., El-Aasser, M., Eds.;

ACS Symposium Series; American Chemical Society: Washington, DC, 1992; Vol. 492, p 28.
(8) Lichti, G.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 269.
(9) Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1987**, *20*, 2922.
(10) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629.
(11) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1323.
(12) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.
(13) Adams, M. E.; Trau, M.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Aust. J. Chem.* **1988**, *41*, 1799.
(14) Lansdowne, S. W.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1344.
(15) Adams, M.; Napper, D. H.; Gilbert, R. G.; Sangster, D. F. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1979.
(16) Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol.* **1976**, *49*, 536.
(17) Nomura, M.; Harada, M. *J. Appl. Polym. Sci.* **1981**, *26*, 17.
(18) Kusters, J. M. H.; German, A. L. To be published.
(19) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2395.
(20) Juang, M. S.; Krieger, I. M. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2089.
(21) Liu, L.; Krieger, I. M. In *Emulsions, Latices and Dispersions*; Becher, P., Ed.; Marcel Dekker: New York, 1978.
(22) Kamel, A. A.-M. Ph.D. Thesis, Lehigh, 1981.
(23) Vanderhoff, J. W.; van den Hul, H. J. *J. Colloid Interface Sci.* **1968**, *28*, 336.
(24) Blackley, D. C.; Haynes, A. C. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 935.
(25) Pohlman, A.; Mill, T. *J. Org. Chem.* **1983**, *48*, 2133.
(26) Lewis, F. M.; Matheson, M. S. *J. Am. Chem. Soc.* **1949**, *71*, 747.
(27) Overberger, C. G.; O'Shaughnessy, M. T.; Shalit, H. *J. Am. Chem. Soc.* **1949**, *71*, 2661.
(28) Petersen, R. C.; Markgraf, J. H.; Ross, S. D. *J. Am. Chem. Soc.* **1961**, *83*, 3819.
(29) Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3225.
(30) Kronberg, B.; Käll, L.; Stenius, P. *J. Dispersion Sci. Technol.* **1981**, *2*, 215.
(31) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935.
(32) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 2459.
(33) Adams, M. E.; Russell, G. T.; Casey, B. S.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624.
(34) Whang, B. C. Y.; Napper, D. H.; Ballard, M. J.; Gilbert, R. G.; Lichti, G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1117.
(35) Lacík, I.; Casey, B. S.; Gilbert, R. G.; Napper, D. H. *Macromolecules*, in press.
(36) Moad, G.; Solomon, D. H. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: London, 1989; Vol. 3, p 97.
(37) Nomura, M. In *Emulsion Polymerization*; Piirma, I. Ed.; Academic: New York, 1982; p 191.
(38) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific: Oxford, U.K., Cambridge, MA, 1990.
(39) Morrison, B. R.; Gilbert, R. G.; Napper, D. H. To be published.
(40) Ahmed, S. M.; El-Aasser, M. S.; Micale, F. J.; Poehlein, G. W.; Vanderhoff, J. W. In *Polymer Colloids* II; Fitch, R. M., Ed.; Plenum: New York, 1980; p 265.
(41) Reid, R. C.; Sherwood, T. K. *The properties of gases and liquids*, 2nd ed.; McGraw-Hill: New York, 1966.
(42) Piirma, I.; Chen, S.-R. *J. Colloid Interface Sci.* **1980**, *74*, 90.
(43) Nomura, M.; Ikoma, J.; Fujita, K. In *Polymer Latexes—Preparation, Characterization and Applications*; Daniels, E. S., Sudol, E. D., El-Aasser, M., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1992; Vol. 492, p 55.

Registry No. I, 144193-13-5; PS, 9003-53-6; PhCH=CH$_2$, 100-42-5.