Desorbed Free Radicals in Emulsion Polymerizations: Effect of Aqueous-Phase Spin Trap

Igor Lacík,[†] Brendan S. Casey, David F. Sangster, Robert G. Gilbert,* and Donald H. Napper

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

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ABSTRACT: Radical loss events by desorption (exit) in seeded styrene emulsion polymerization systems are studied by observing (1) the relaxation behavior when polymerization is initiated by γ radiolysis and then rapidly removed from the radiation source and (2) the same radiolysis relaxation experiment with the addition of an aqueous-phase free-radical trap (Fremy's salt). The results are quantitatively consistent with desorbed free radicals being rapidly terminated by Fremy's salt before there is any opportunity for them to reenter another particle and with the transfer–diffusion model for exit. The Fremy's salt technique is a general one which should be able to be used to establish the fate of free radicals in a wide range of emulsion polymerization systems.

Introduction

There is now irrefutable evidence that the exit (or desorption) of free-radical activity in an emulsion polymerization can be kinetically significant even for relatively insoluble monomers such as styrene.[1-4] For many important emulsion polymerization systems, exit is a major (or the only) cause of the loss of free-radical activity inside a particle: examples include vinyl acetate,[5] vinyl chloride,[6] butadiene,[7] and (for particles of swollen radius less than 85 nm) styrene,[1,4] methyl methacrylate,[8] and indeed any emulsion polymerization system where the particles are sufficiently small. Moreover, a knowledge of the mechanism of exit and of the subsequent fate of the desorbed free radical is important in unraveling the complexities of particle nucleation.[9-11] An understanding of the mechanism for exit is therefore an important component in the design and control of latex properties and polymer production in such systems.

It is generally accepted that the actual desorption process is governed by the following events:[12-16] (1) transfer of free-radical activity inside the latex particle to a species of sufficiently high aqueous-phase solubility that exit may occur; (2) diffusion of the resulting monomeric free-radical species through the particle, across the aqueous-phase/particle interface and away from the particle; and (3) propagation of the monomeric free radical inside the particle before exit can occur (resulting in a species so insoluble that exit is kinetically unlikely). However, as will be explained in detail later in this paper, the observed polymerization rate in such systems is governed not only by these events but also by the fate of the desorbed free radical:[3,14,15,17-19] i.e., by inter- as well as intraparticle processes. Because it is difficult to separate the intra- and interparticle events in conventional emulsion polymerization systems, it is hard to establish the validity of proposed mechanisms.[20] The objective of the present paper is to establish and to apply means of carrying out this mechanistic unraveling for these complex kinetic processes.

The basic origin of the complexity of exit kinetics is the plethora of possibilities for the fate of the desorbed free radical. These are as follows: (1) aqueous-phase termination, either with another desorbed free radical (homotermination) or with a free radical derived directly from the initiating species (heterotermination); (2) aqueous-phase propagation of the desorbed species (which, for a monomer of low water solubility such as styrene, is unlikely for the uncharged free radical resulting from transfer within the particle and which causes free-radical loss by desorption; note that this *exiting* species is different from the charged radical species in the aqueous phase arising from initiators which *enter* the particle[21]); or (3) reentry into another particle. In this latter case, there are then several further possibilities for the fate of the reentered free radical: (a) termination (if another free radical is present within the entered particle); (b) propagation (to form a species which is unlikely to exit); or (c) reexit. Moreover, it is possible, and indeed likely, that several of these fates may be simultaneously kinetically significant for the radicals in any particular system.

Because of the complexity of these processes, we use the following criteria to select a suitably simple system for study and for design of the appropriate methodology: (1) So as to avoid the complexities of particle formation, we choose seeded systems for study and ensure that there is no secondary particle formation or droplet polymerization for the runs used for kinetic interpretation, both of which are checked in these experiments by electron microscopy. (2) The system should be such that exit is the only significant free-radical loss event from the particles, i.e., where termination is not rate-determining. Hence we choose a "zero–one" system[1] (Smith–Ewart[22] case 1 or 2), wherein there can be no more than one free radical per particle, the conditions being such that entry of a second free radical causes instantaneous termination. (3) Because of the complexities inherent in the aqueous-phase kinetics which govern the *entry* of free radicals into latex particles (i.e., the initiator efficiency),[21] we choose to study a system whereby the initiation is by γ radiolysis. Such systems have the advantage[4,23] that the source of free radicals can be removed essentially instantaneously and the kinetics then monitored in the "relaxation mode". This means that there are no new free radicals produced, except for a relatively small thermally generated contribution[1,4] (which presumably arises from reactions on or near the surface of the particles). That is, we choose a system where entry is minimal. (4) So as to eliminate (or at least minimize) the complications arising from the aqueous-phase kinetics of a desorbed free radical, we employ here (apparently for the first time in the study of emulsion polymerization kinetics) Fremy's salt [potassium

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[†] Present address: Polymer Institute, Slovak Academy of Sciences, 84236 Bratislava, Czech and Slovak Federative Republic.

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nitrosodisulfonate, $K_2NO(SO_3)_2$] as a free-radical trap and examine its effect on the relaxation kinetics. Fremy's salt (henceforth denoted FS) should be essentially soluble only in the aqueous phase and so *in principle* should "instantaneously" terminate any free radical which has completely desorbed (i.e., escaped from its parent particle without reentering that particle), hence eliminating interparticle kinetic events while having no effect on the intraparticle kinetics. It is essential to test whether or not such ideal behavior in fact occurs, as there are clearly some possible complications; e.g., FS might react with free radicals near the particle surface before they exit, or FS might prevent reentry into the *parent* particle during the quasi-equilibrium process of diffusing away from the parent particle. (5) We choose a system for which there are already extensive experimental data and concomitant mechanistic understanding, viz., the seeded emulsion polymerization of styrene.

The basic technique to be employed is as follows. We carry out a seeded emulsion polymerization using γ-radiolysis initiation and remove the polymerizing vessel from the radiation source. We then inject FS, under conditions so that mixing and reequilibration is rapid compared to the overall relaxation time in the same system after removal from the course in the absence of FS. The effects of FS on the relaxation are then examined.

Theory of Desorption Kinetics

We present here an outline of the essential features that govern the kinetics of exit; full details have been presented elsewhere.[19] At the outset, we note that there is a nontrivial notational problem in this outline, inasmuch as (1) there is as yet no standard notation for the rate coefficients for the various processes under consideration, and (2) it will be seen that different mechanistic postulates can give rise to rate equations that are formally identical (e.g., eqs 7 and 8 below). With regard to point 1, we adhere as closely as possible to the notation of Ugelstad and Hansen[16] and otherwise adopt a notation that is mnemonically convenient (e.g., k_{cr} refers to the rate coefficient for the process in which there is "complete reentry" of desorbed free radicals). For point 2, we always choose to have different notation for rate coefficients for different processes, even though this leads to more than the minimal number of rate coefficients.

As stated, we confine our attention to a zero–one system and consider the time evolution of the average number of free radicals per particle, $\bar{n}$ (since this is a zero–one system, $\bar{n} \leq 1/2$). This is related to the fractional conversion x by

$$\mathrm{d}x/\mathrm{d}t = (k_p C_M N_c / n_M N_A)\bar{n} \tag{1a}$$

where k_p is the propagation rate coefficient, C_M is the monomer concentration in the latex particles, N_c is the particle concentration (per unit volume of reaction medium), n_M is the initial number of moles of monomer per unit volume of reaction medium, and N_A is the Avogadro constant. Equation 1a is applicable in both interval II (i.e., in the presence of monomer droplets) and interval III (no monomer droplets present and hence C_M decreases as polymerization proceeds). A simplification occurs in the latter case, when $C_M = (1 - x)C_M^0$, C_M^0 being the monomer concentration at $x = 0$, and one has as well[24]

$$-\frac{\mathrm{d}\ln(1-x)}{\mathrm{d}t} = \frac{k_p C_M^0 N_c}{n_M N_A}\bar{n} \tag{1b}$$

Denoting by N_i the fraction of particles containing i free radicals, for a zero–one system one has $\bar{n} = N_1$ (where we have normalized the N_i so that $N_0 + N_1 = 1$). Because of the compartmentalized nature of an emulsion polymerization system (where entry into an N_1-type particle causes instantaneous termination), we have the Smith–Ewart equations[22] for zero–one kinetics:[3]

$$\mathrm{d}N_0/\mathrm{d}t = -\rho N_0 + (\rho + k)N_1 \tag{2}$$

$$\mathrm{d}N_1/\mathrm{d}t = \rho N_0 - (\rho + k)N_1 \tag{3}$$

where ρ is the phenomenological rate coefficient for entry of a free radical into a particle and k is that for exit. One thus has

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho - (2\rho + k)\bar{n} \tag{4}$$

This equation is deceptively simple, since the complications of the aqueous-phase kinetics, including those governing the fate of exited free radicals, mean that both ρ and k can be quite complex functions of $\bar{n}$, N_c, C_M, and initiator concentration.[3,19] For the purposes of the present paper, we examine various limits of eq 4, for simplifying cases of the fate of exited free radicals. For this purpose, we replace the phenomenological exit rate coefficient k with appropriate radical-loss rate coefficients which specifically incorporate two important limiting cases of the exit mechanism; the radical-loss rate coefficients so defined (the definition depending on the chosen limiting case) will be independent of $\bar{n}$, unlike the phenomenological k of eq 4 (however, these rate coefficients may depend upon N_c, C_M, and initiator concentration). Here we present these simple limiting cases; complete derivations are given elsewhere.[19]

The radical-loss mechanism is postulated to be transfer to monomer to form a monomeric free radical, which can escape completely into the aqueous phase if it diffuses away from the particle before it propagates. The desorption rate coefficient k_{ex} is then given by[14,16,19]

$$k_{ex} = k_{tr} C_M \frac{k_{dm}}{k_{dm} + k_p^1 C_M} \equiv k_{tr} C_M P_{es} \tag{5}$$

where k_{tr} is the rate coefficient for transfer (to monomer, in the absence of added soluble chain-transfer agent), k_p^1 is the propagation rate coefficient of a *monomeric* free radical (which may be significantly different from k_p, the propagation rate coefficient for a macroradical), and P_{es} is the probability of diffusional escape (compared to the alternative fate of a monomeric free radical inside a particle, which is to propagate and thus remain inside the particle). In the present series of experiments, we are interested in systems where diffusion of a monomeric free radical inside a particle is much faster than its diffusion away from the particle through the aqueous phase. The escape rate coefficient (k_{dm}) giving the rate of diffusion away from a particle, is then given by

$$k_{dm} = (3D_{aq}/r_s^2)(C_{aq}/C_M) \tag{6}$$

In eq 6, r_s is the swollen radius of the particle, D_{aq} is the diffusion coefficient of a monomeric free radical in the aqueous phase, and C_{aq} and C_M are the equilibrium solubilities of monomer (and hence of monomeric free radical) in the aqueous and particle phases, respectively, under the particular conditions of the system. Equation 6 (and extensions which include taking into account systems where diffusion within the particle may be rate-determining) can be simply derived[16] by noting that (for systems such as those considered here) the diffuse rate of a monomeric free radical *inside* the particle is very rapid and relating the capture rate coefficient of an aqueous-phase monomeric free radical (k_e), calculated by the Smoluchowski equation ($k_e = 4\pi D_{aq} r_s$) and the escape rate coefficient (k_{dm}) by microscopic reversibility (since these two processes are exactly the reverse of each other); the factor C_{aq}/C_M in eq 6 arises simply from the equilibrium constant, which relates the forward and reverse rate coefficients.[25] The validity of the Smoluchowski equation for reentry (capture) of these uncharged species is justified on the grounds that there does not seem to be any barrier to their entry, especially in light of recent results[21] that show that entry of a charged oligomeric species is so rapid as not to be rate-determining. It should be noted that eq 6, being a steady-state flux, takes specific account of the possibility that a desorbed free radical, after escaping through the surface, reenters its parent particle.

In deriving our simple limiting cases for exit, we confine ourselves here to γ-radiolysis relaxation systems. The only contribution to the entry rate coefficient ρ is then the background thermal component ρ_0, a first-order rate coefficient which is assumed completely independent of $\bar{n}$. Next, we consider two possible limiting cases for the fate of exited free radicals in a γ-relaxation experiment:

(1) Complete Aqueous-Phase Termination. In this limit, there is assumed to be no kinetic effect from the desorbed free radicals: i.e., the only possible fate of an exited free radical in a γ-relaxation system (when there are no free radicals formed in the aqueous phase after removal from the ^{60}Co source) is to undergo aqueous-phase termination with another exited free radical or with an aqueous-phase spin trap such as FS. The overall kinetics are then given simply by

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho_0 - (2\rho_0 + k_{ct})\bar{n} \qquad (7)$$

where the desorption rate coefficient k_{ct} (for "complete termination") of eqs 5 and 6 has replaced the phenomenological k of eq 4. Note that this result can also be obtained in terms of the more primitive treatment of exit[3,18] using the "fate parameter" α by putting $\alpha = 0$. If eq 7 were to be obeyed, then the value of k_{ct} would be expected to be equal to that of the model-based k_{ex} of eqs 5 and 6.

If the experiment were to be carried out in the presence of an aqueous-phase free-radical trap, which terminates all radicals that completely escape from the particle (but still allows the desorbed radical to reenter its parent particle), then the system would be expected to obey a relation of the same form as eq 7, with the desorption rate coefficient therein denoted by k_{st} (for "spin trap"):

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho_0 - (2\rho_0 + k_{st})\bar{n} \qquad (8)$$

with $k_{st} = k_{ex}$. If on the other hand the radical trap instantly terminates the monomeric free radical *as soon as it emerges from the particle* (i.e., before it has time to reenter its parent particle), then eq 8 would still hold but now the escape probability P_{es} is much closer to unit in eq 5; i.e., $k_{st} \approx k_{tr}C_M$ (the equality holding if every free radical which enters the aqueous phase is terminated by FS before it has a chance to reenter its parent particle). In general, in the presence of an aqueous-phase spin trap, eq 7 should hold with $k_{tr}C_M \geq k_{st} \geq k_{ct} = k_{ex}$. It is important to note that ρ_0 and k_{ct} in eq 7 are independent of $\bar{n}$ (although they may depend on other quantities such as C_M), in contrast to eq 4. Hence our expectation for the present system with the addition of FS is that eq 7 should hold, with $k_{tr}C_M \geq k_{st} \geq k_{tr}C_M P_{es}$.

(2) Complete Reentry and Minimal Reexit. In this limit, the fate of an exited free radical is to reenter another particle and to remain inside without reexiting (i.e., it is supposed to propagate sufficiently rapidly inside the particle that it cannot reexit); inter alia, this implies that instantaneous termination will occur if the entered particle already contains another free radical. Denoting this limit for the loss rate coefficient by k_{cr} (for "complete reentry"), this leads to the following replacement for eq 4:

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho_0 - 2\rho_0\bar{n} - 2k_{cr}\bar{n}_2 \qquad (9)$$

(a result which can be obtained in terms of the more primitive treatment of exit[3,18] using the fate parameter by putting $\alpha = 1$). Again, in eq 9, ρ_0 and k_{cr} are independent of $\bar{n}$. Moreover, in this limit, $k_{cr} = k_{tr}k_{dm}/k_p^1$.

Hence our expectation is that the loss rate coefficient measured after injection of FS, which will be found from the data using eq 8, when compared to that in the absence of FS, which will be found from the data using *either* eq 7 (if the system is such that desorbed free radicals undergo complete termination in the aqueous phase) *or* eq 9 (if the system is such that desorbed free radicals undergo complete reentry into another particle), should obey the inequalities

$$k_{cr}, k_{ct} \leq k_{st} \leq k_{tr}C_M \qquad (10)$$

An important objective is to see which (if any) of the two alternative mechanisms for radical loss dominates in a particular system. If either one is dominant, then we would have $k_{cr} = k_{tr}k_{dm}/k_p^1$ (if the only fate of an exited free radical is to reenter a random particle) or $k_{ct} = k_{ex}$ (if the only fate of an exited free radical is to terminate in the aqueous phase). Obviously, both mechanisms may be kinetically significant, in which case neither eq 7 nor 9 would provide a proper description of the data (although either or both might be able to provide an apparent fit to experimental data of limited precision and/or range of conditions), and a more complex treatment[19] would be necessary.

The objective of the present study is to test the ideas on the exit mechanism encapsulated in eqs 7–10. The quantities k_{ct}, k_{cr}, ρ_0, and k_{st} in those equations can be obtained from conversion–time relaxation data in a number of ways. The simplest of these is to employ the "slope-and-intercept" method used in earlier work.[3,18] This treatment is a generalization (although certainly not a complete one[19]) of eqs 7 and 9, expressing them in terms of the fate parameter α; as stated, eq 7 is obtained with $\alpha = 0$ and eq 9 with $\alpha = 1$, and thus data fitting is through eqs 7–9 of Whang et al.[18] The slope-and-intercept method gives a simple means of fitting conversion–time data (by examining the long-time behavior) given an assumed value of α. As is shown later, the use of a water-soluble spin trap leads to $\rho_0 = 0$ and $\alpha = 1$. For this particular case, the abovementioned equations of Whang et al. are mathematically indeterminate; however, the appropriate solution to eqs 2 and 3 can be trivially derived for this special case.[19]

An alternative to the slope-and-intercept method (which uses the *integrated* form of eqs 7–9) is to examine the *differential* form of these equations directly: i.e., the dependence of the experimental $\mathrm{d}\bar{n}/\mathrm{d}t$ on $\bar{n}$ (eq 7 or 8) or $\bar{n}^2$ (eq 9). While these should in principle yield a sensitive probe of the order of the radical loss process, the use of the second derivative ($\mathrm{d}\bar{n}/\mathrm{d}t \propto \mathrm{d}^2x/\mathrm{d}t^2$) of experimental data means that such a treatment involves very noisy data. Thus while we shall present fits using this "differential" method (in Figures 4 and 6), the large noise inherent in this procedure makes such fits suggestive rather than confirmatory, and such fits can only be used in conjunction with the "integral" method, which we now describe, which is subject to much less noise.

Data fitting using the integrated form of eqs 7–9 (through the slope-and-intercept method, eqs 7–9 of Whang et al.) places approximately equal emphasis on the whole-time evolution of the conversion, while data fitting using the differential form (i.e., from a plot of $d\bar{n}/dt$ against $\bar{n}$ or $\bar{n}^2$) places most emphasis on the early-time behavior. However, results obtained from these two alternative approaches (which we denote the integral and differential methods, respectively) should be the same within the uncertainty of each; this will provide an important consistency test for the data interpretation employed.

Experimental Section

Styrene (Aldrich) was purified by distillation under reduced pressure. Aerosol MA (sodium dioctylsulfosuccinate, Cyanamid Australia) was used for seed preparation as an 80% solution in water; sodium dodecyl sulfate (SDS, Aldrich, used without further purification) was employed as surfactant for seeded runs (inter alia because this surfactant reduces the incidence of secondary particle formation). The water-soluble inhibitor Fremy's salt (Aldrich) was used without purification. All other chemicals were of analytical grade; water was doubly distilled, the second time from permanganate. The seed latex (BRM70) was prepared and cleaned (by dialysis) using the method described by Lansdowne et al.[4] with the following recipe: styrene 131 g, H_2O 373 g, Aerosol MA 6.6 g, $NaHCO_3$ 0.5 g, $K_2S_2O_8$ 0.5 g. The unswollen radius of the resulting monodisperse latex, measured by electron microscopy with internal standard,[1] was 57 nm; it has been established[1] that the kinetics of styrene-seeded emulsion polymerization at 50 °C under such conditions are indeed zero–one. The swollen radius of the latex particle at saturation monomer concentration (5.8 mol dm^{-3} [1]) is 84 nm. The γ-initiated seeded polymerization of styrene employed a ^{60}Co source giving a highest dose rate of 190 mGy s^{-1}; the experimental setup for removal of a sample from the source has been described previously.[4] The rate of polymerization was measured dilatometrically. Varying radiation dose rates were employed; the radical-loss rate coefficient should of course be independent of initial conditions, i.e., the initial value of $\bar{n}$, and thus use of different dose rates gives a check on experimental uncertainty and consistency of interpretation.

Kinetic runs were carried out in interval II and interval III at 50 °C for a seeded polymerization system which contained $\sim 1 \times 10^{16}$ particles per dm^3 of emulsion. The initial weight fraction of polymer in particles was 0.36 for interval II and ca. 0.4 for interval III. SDS was added to ensure the stability of the swollen particles and was kept below its cmc. Checking for secondary nucleation was by measurement of particle number after kinetic runs using electron microscopy.

This work requires injection of FS into the polymerization vessel at the "moment" when the sample cavity is removed from the source. FS is rather reactive,[26] and we found that its aqueous solution lost is violet color after a few minutes and had no reproducible effect on the course of polymerization after injection. Instead of using a solution of FS for injection, the following method was devised to allow for injection of solid FS (so as to avoid any chemical change prior to injection of a previously prepared solution). A known amount of solid FS ($\sim 10^{-4}$ mol dm^{-3} of the emulsion volume in reactor) was weighed into the syringe connected through the needle, two-way tap, and polyethylene tubing with the reaction vessel placed into the sample cavity of the γ-source. During the "in-source" steady-state polymerization, a small volume (less than 0.1 cm^3) of polymerizing emulsion was pulled into the syringe to dissolve the FS crystals. As soon as the crystals were dissolved (0.5–1 min), the sample cavity was removed from the source and a part of the syringe contents (emulsion containing FS solution) was injected (via a septum) into the reaction vessel. This procedure disturbed the thermal equilibrium of the system, which reequilibrated after 5–10 min. The decay of the polymerization rate was then measured. As a check for any artifacts resulting from the injection procedure, a blank injection of KCl, at the same concentration as that of FS, was performed in the same way. Results are shown in Figure 1.

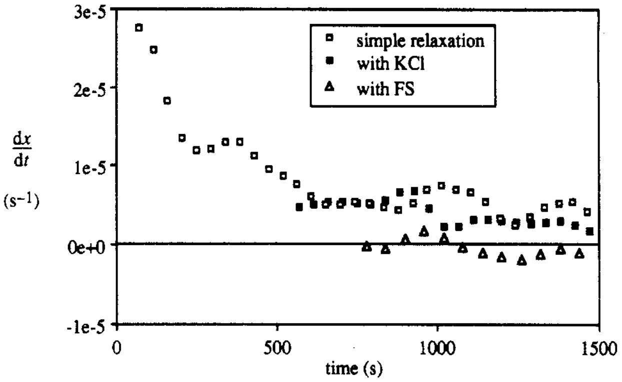

Figure 1. Relaxation rate in γ-radiolysis-initiated seeded emulsion polymerization of styrene at 50 °C, after removal from the free-radical source, for three different conditions: without addition of aqueous-phase spin trap, with the injection of KCl (as a blank), and with the injection of Fremy's salt. Note samples where salt was injected take ~500 s for reequilibration.

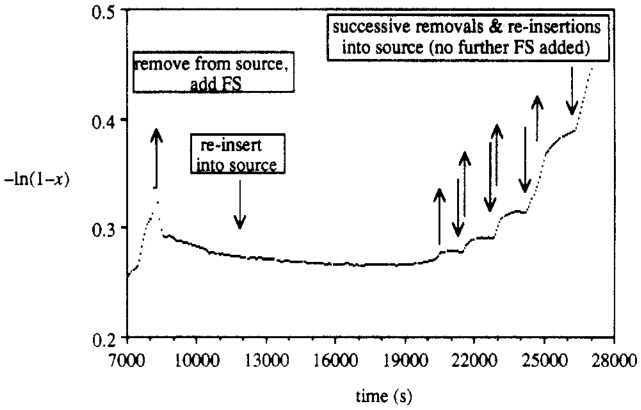

Figure 2. Conversion, as $-\ln(1 - x)$ (appropriate measure of conversion for this interval III run), as a function of time for a system where FS is injected into the system, and the system is reinserted into the source and removed a number of times without further addition of FS. Second, third, and fourth removals clearly lead to essentially zero rate of polymerization. Apparent decrease in conversion after addition of FS until ca. 18 000 s is an artifact arising from thermal reequilibration and slight temperature drift; this results in no significant error in subsequent relaxations.

As shown in Figure 2, it was found that when the vessel is inserted back into the source after relaxation following addition of FS, in-source polymerization still takes place, albeit at a reduced rate. This polymerization rate in the presence of the aqueous-phase spin trap gradually increases with time, depending on the dose rate and the initial FS concentration. Upon subsequent removal from the source, the final rate after relaxation is still zero (until very late in the run, after very long exposure to γ radiolysis), showing that a sufficient amount of spin trap to eliminate the thermal contribution to entry is still present even after reinsertion into the radiation source. This second removal then allows us to follow relaxation in the presence of spin trap *without having to add more spin trap and wait for thermal reequilibration.* This technique thus enabled us to follow relaxation kinetics that occur on a much shorter time scale than that of thermal reequilibration.

Results and Discussion

Figure 1 shows typical relaxation experiments at 50 °C. Three relaxations are presented: without any injection, relaxation after injection of KCl, and relaxation after injection of FS; in each case, time $t = 0$ is when the reaction vessel was removed from the source. The relaxation without any injection shows the normal behavior observed in such experiments; at long times a nonzero thermal steady-state value is attained. When KCl is injected, the decay of the polymerization rate becomes almost identical

Table I
Radical-Loss and Background Thermal Rate Coefficients (10^{-3} s^{-1}) from Relaxation Experiments (No Added Spin Trap)[a]

	run									
	16	21	26	31	41a	41b	41c	42	46a	46b
N_c (10^{15} dm^{-3})	8.9	9.0	9.3	9.0	9.5			9.4	11	
dose rate (mGy s^{-1})	95	95	190	190	6			190	6	
$\bar{n}_{\text{initial}}$	0.50	0.50	0.50	0.52[b]	0.33	0.41	0.45	0.45	0.29	0.38
$\bar{n}_{\text{SS}}$	0.04	0.07	0.03	0.08	0.11	0.13	0.11	0.07	0.12	0.11
w_p	0.36	0.36	0.36	0.36	0.42	0.52	0.59	0.43	0.44	0.50
first order										
ρ_0										
integral	0.16	0.25	0.19	0.28	0.65	0.75	0.60	0.51	0.55	0.59
differential	0.20	0.13	0.17	0.27	0.66	0.70	0.88	0.21	0.46	–
k_{ct}										
integral	4.2	3.6	3.4	3.0	4.5	4.4	4.0	6.1	3.3	4.0
differential	2.3	1.7	1.7	3.6	4.0	3.9	5.1	3.2	4.6	–
second order										
ρ_0										
integral	0.03	0.06	0.02	0.08	0.27	0.30	0.27	0.14	0.25	0.23
differential	0.01	0.04	–	0.00	0.25	0.23	0.28	0.09	0.27	–
k_{cr}										
integral	9.7	6.6	7.8	5.2	8.1	7.0	6.4	12	6.1	6.9
differential	7.5	4.7	4.5	5.7	8.0	7.0	9.4	11	10	–

[a] $\bar{n}_{\text{initial}}$ value of $\bar{n}$ just before removal from source; $\bar{n}_{\text{SS}}$, steady-state (long-time) value of $\bar{n}$ achieved after relaxation; w_p, weight fraction of polymer in particles during relaxation. "First order" refers to value obtained using eq 7; "second order" refers to value obtained using eq 9; "integral" refers to values obtained by data reduction using slope-and-intercept method (integrated form of eqs 7 and 9); "differential" refers to those from a plot of $d\bar{n}/dt$ vs $\bar{n}$ (eq 7) or $\bar{n}^2$ (eq 9). Multiple results for runs 41 and 46 are from multiple insertions and relaxations. Dashed entries are for results where data are so noisy that application of the differential method leads to an unphysical negative result. [b] Zero–one data processing methods invalid if $\bar{n} > 0.5$; however, these data are included because uncertainty of ±1 nm in particle radius gives a ±0.03 uncertainty in $\bar{n}$, suggesting that in fact $\bar{n} \leq 0.5$ for this run; the consistency of the radical-loss rate coefficients for run 31 with those from runs where $\bar{n} \leq 0.5$ suggests that run 31 also obeys zero–one conditions.

with the previous relaxation (i.e., in the absence of injection) after the system has reestablished thermal equilibrium. This establishes that the physical procedure of injection creates no artifact apart from briefly disturbing the thermal equilibrium.

When FS is injected, the final (background thermal) rate of polymerization falls to zero within the sensitivity of the present experimental design. This could be an important observation concerning the origin of the thermal background, although this feature is not further investigated in the present study.

Our aims are first to test the hypothesis that the first-order mechanism for radical loss (eq 8) indeed fits the data from the FS experiments. We then wish to see if either or both mechanisms (i.e., eq 7 or 9) fit the data in the absence of FS and then to compare the radical-loss rate coefficients so obtained with that from the FS result: i.e., to test inequality 10. The entry and radical-loss rate coefficients determined from the relaxations without FS are summarized in Tables I and III. These cover a wide range of experimental conditions–high/low dose rate, interval II/interval III, and different initial weight fraction (w_p) of polymer. Both data reduction methods discussed above were applied to the data. Results are shown in Tables I and III.

The first test of consistency is that the values of the rate parameters obtained by the differential and integral methods should be the same, within experimental uncertainty, for a given run. Inspection of the results displayed in Tables I and II shows that this is indeed the case. As foreshadowed, results obtained using the differential method have higher uncertainty, and indeed some of the values of ρ_0 so obtained were negative, which is unphysical.

Table II
Radical-Loss and Background Thermal Rate Coefficients (10^{-3} s^{-1}) from Relaxation Experiments with Added Spin Trap[a]

	run			
	31	43	46a	46b
N_c (10^{15} dm^{-3})	9.3	9.3	11	
dose rate (mGy s^{-1})	190	190	6	
$\bar{n}_{\text{initial}}$	0.47	0.52[b]	0.18	0.29
$\bar{n}_{\text{SS}}$	0	0	0	0
w_p	0.36	0.43	0.57	0.58
first order				
ρ_0				
integral	0	0	0	0
differential	–	0.06	0.15	0.01
k_{st}				
integral	7.8	12	7.4	8.0
differential	11	15	5.3	4.7
second order				
ρ_0				
integral	0	0	0	0
differential	–	–	0.1	–
k_{cr}				
integral	–	–	–	–
differential	6	34	50	35

[a] Notation as in Table I. Dashed entries for differential method, data so noisy that unphysical result obtained; dashed entries for integral method, functional form could not give adequate fit to data (see Figure 5). Multiple entries for run 46 are from multiple insertions. [b] $\bar{n}$ apparently >0.5; see note in Table I.

The rate coefficients for radical-loss values obtained here may be compared with those obtained previously for a latex of swollen radius $r_s = 71$ nm.[4] These earlier values were for a latex of a size different from that in the present studies, but can be "rescaled" using eq 6 (i.e., multiplied by the square of the ratio of the swollen radii), a scaling which has been verified experimentally.[1] These size-rescaled values (i.e., predicted for a latex with $r_s = 71$ nm, from the values in Table III) are 11×10^{-3} s^{-1} using second-order, and 6×10^{-3} s^{-1} using first-order kinetics. However, the values reported[4] for a latex with $r_s = 71$ nm were 1.5×10^{-3} and 1.1×10^{-3} s^{-1}, using second- and first-order kinetics, respectively. The difference between the two results lies outside experimental uncertainty. We are unable to explain this discrepancy; it may arise from either experimental error in the early studies (which were the first to be carried out with the technique) or the presence

Table III
Data from Tables I and II, as Comparison of Radical-Loss Rate Coefficients (s^{-1})[a]

Runs with Added FS	
first-order fit	
k_{st}	
integral	$(9 \pm 2) \times 10^{-3}$
differential	$(9 \pm 5) \times 10^{-3}$
Runs without FS	
first-order fit	
k_{ct}	
integral	$(4 \pm 1) \times 10^{-3}$
differential	$(3 \pm 1) \times 10^{-3}$
second-order fit	
k_{cr}	
integral	$(8 \pm 2) \times 10^{-3}$
differential	$(8 \pm 2) \times 10^{-3}$

[a] From relaxation experiments with no added spin trap, interpreted with second-order kinetics (k_{cr}) and with first-order kinetics (k_{ct}), and from relaxation experiments with added spin trap, interpreted with first-order kinetics (k_{st}). "Integral" refers to values obtained by data reduction using the slope-and-intercept method (integrated form of eqs 7–9); "differential" refers to those from a plot of $d\bar{n}/dt$ vs $\bar{n}$ (eq 7 or 8) or $\bar{n}^2$ (eq 9).

of an adventitious chain-transfer agent such as buried surfactant. The surfactants used in these studies are known[27] to have relatively large chain-transfer constants; this could affect the radical-loss rate coefficient, as is apparent from eqs 5 and 6. That a chain-transfer agent can have a large effect on the radical-loss rate coefficient has also been verified experimentally.[28] This question requires further investigation. However, the present results are from a large series of experiments, are quite reproducible over the present wide range of dose rates and w_p values, are the same for both intervals II and III, and are therefore considered both reliable and consistent, including any effect which may arise from buried surfactant, etc.

Having established the consistency of the two methods of data fitting, some minor points need to be considered. In data fitting using the differential method for eq 9, the fit was to a simplified version of this equation, viz., $d\bar{n}/dt = \rho_0 - 2k_{cr}\bar{n}^2$: i.e., the first-order term was ignored (this will be valid if $\rho_0\bar{n}$ is appreciably less than $k_{cr}\bar{n}^2$, an approximation whose validity can be subsequently verified from the resulting fits). Attempts to include both a first- and a second-order term (i.e., a three- rather than a two-parameter fit) gave statistically meaningless results because of the noise inherent in the data. This approximation of ignoring the first-order term is unnecessary with the integral method.

Next, it is apparent from the data in Tables I and II that the "background thermal" rate coefficient ρ_0 decreases with the flux of the ^{60}Co source. While the chemical nature of this background thermal source of free radicals is unknown, one can postulate that it might be due, for example, to a peroxy compound at the particle surface (perhaps arising from persulfate decomposition byproducts formed during preparation of the seed). If so, it is not unreasonable to suppose that such species might be destroyed by exposure to the products of a high flux of γ rays interacting with water.

As a major result of the present studies, we now attempt to see which of eqs 7–9 gives a better fit to the data, in the absence and presence of spin trap. Typical fits with both models are shown in Figures 3–6 (although these show only the results of a single run, all runs listed in Table I were subjected to these analytical procedures).

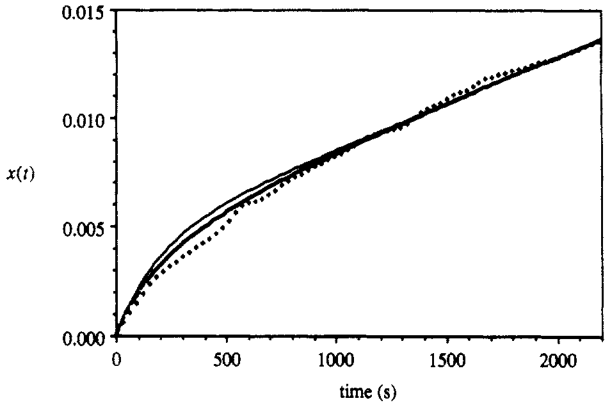

Figure 3. Conversion as function of time for run 21: ordinary γ relaxation (no added FS), showing fit with integrated forms of eqs 7 and 9. Run was in interval II (in the presence of monomer droplets), hence data plotted as conversion against time. Points, experiment; thin line, first-order fit (using integral of eq 7); thick line, second-order fit (using integral of eq 9).

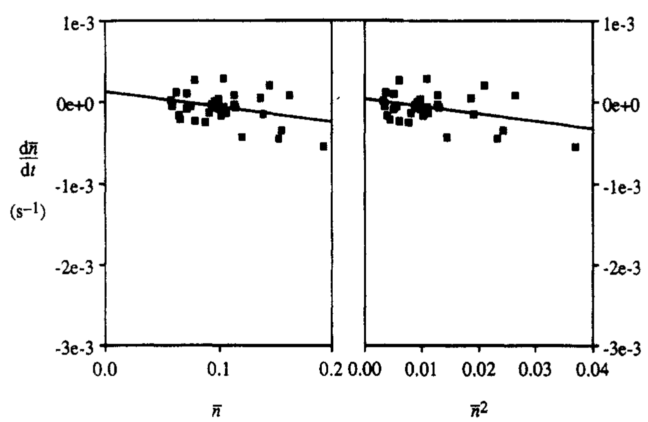

Figure 4. Rate of change of free-radical concentration as a function of time for run 21: ordinary γ relaxation (no added FS), showing fit to differential forms of eqs 7 ($d\bar{n}/dt$ vs $\bar{n}$) and 9 ($d\bar{n}/dt$ vs $\bar{n}^2$). Points, experiment; lines, least-squares fits to these equations.

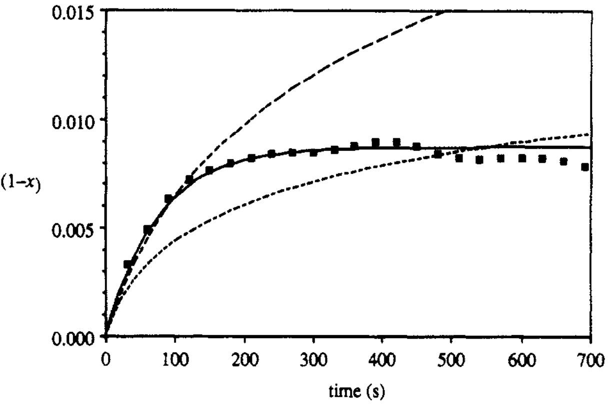

Figure 5. Conversion as function of time for run 43, in which spin trap (FS) was added, showing fit with integrated forms of eqs 8 and 9. Run was in interval III (absence of monomer droplets), hence data plotted as $-\ln(1-x)$ against time. Points, experiment; full line, first-order fit (using integral of eq 8); broken lines, second-order fits (using integral of eq 9). This model cannot fit the data properly, the fits shown in the figure either giving accord with the experimental rate at long times but a very poor fit of the early-time results ($k_{cr} = 3.5 \times 10^{-2}$ s^{-1}) or vice versa ($k_{cr} = 1.4 \times 10^{-2}$ s^{-1}).

We first consider which of eq 7 or 9 provides a better fit for relaxation data in the absence of added free-radical trap (Figures 3 and 4). It appears that the second-order mechanism, eq 9 (i.e., complete reentry of desorbed free radicals), often provides a slightly better fit than does the alternative. However, the data are not sufficiently free from noise for this conclusion to be unambiguous. Indeed,

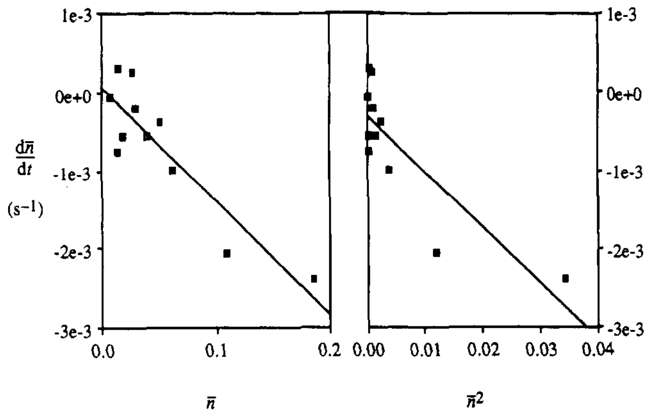

Figure 6. Rate of change of free-radical concentration as function of time for run 43, in which spin trap (FS) was added, showing fit to differential forms of eqs 8 ($d\bar{n}/dt$ vs $\bar{n}$) and 9 ($d\bar{n}/dt$ vs $\bar{n}^2$). Points, experiment; lines, least-squares fits to these equations.

the better fits to eq 9 rather than to eq 7 shown for a particular case in Figures 3 and 4, although typical, are not invariably found: In the runs in the present study, there was one (run 31) where the first-order fit was apparently better. One reason that the data cannot unambiguously distinguish if either first- or second-order kinetics (or both) are applicable to this system is that eq 9 contains both first- and second-order terms, and the first-order component ($\rho_0\bar{n}$) takes on values which are comparable to those of the second-order component ($2k_{cr}\bar{n}^2$).

With the addition of FS, the situation is much more clear-cut. It is apparent from Figure 5 that only the first-order kinetics are able to provide an adequate fit to the data. It is noteworthy that one of the reasons that these data are able to refute the second-order model unambiguously is that, in the presence of FS, the value of ρ_0 is essentially zero (Table II), and hence there is no first-order component in the second-order case, eq 9: This contrasts with the situation in the absence of a radical trap.

Hence the first conclusions to be drawn from the data are that, in the presence of a free-radical trap, all desorbed free radicals are terminated in the aqueous phase. Moreover, from the value of k_{st} so obtained (9×10^{-3} s^{-1}) and the value for $k_{tr}C_M$ (5×10^{-2} s^{-1}, found using the value of $k_{tr}/k_p = 3.5 \times 10^{-5}$ [29] and $k_p = 260$ dm^3 mol^{-1} s^{-1} [1]), it is apparent that inequality 10 is obeyed and that most, if not all, of the free radicals which escape from the particle are trapped by the FS only when they have diffused away from their parent particle. If not, we would not have $k_{st} \ll k_{tr}C_M$.

Next, we compare the values of the radical-loss rate coefficient found in the absence of FS (k_{ct} and k_{cr}) with the restrictions of inequality 10. As stated, the present data are unable to provide evidence as to whether either or both of the loss mechanisms in the absence of spin trap (complete reentry or complete aqueous-phase termination) are applicable to the present system. It can be seen from the data collected in Table III that inequality 10 is indeed obeyed. Moreover, it is apparent that the radical-loss rate coefficient obtained using second-order kinetics (k_{cr}) is in close accord with that obtained in the presence of FS (k_{st}). This could be interpreted as implying that both are equal to the appropriate limit of k_{ex} of eqs 5 and 6: i.e., (1) FS only traps desorbed free radicals when they have diffused a sufficient distance from their parent particle for eqs 5 and 6 to be applicable (i.e., the conditions here are such that a desorbed free radical may reeneter its parent particle, but not a different particle, in the presence of FS), and (2) in the absence of a spin trap, all desorbed free radicals reenter a particle, so that eq 9 is applicable and moreover that the desorption rate is governed by the transfer–diffusion mechanism (so that $k_{cr} = k_{ex}$). However, this interpretation uses false logic; it can be seen from inequality 10 that the data are merely *consistent* with these suppositions, but *cannot refute*[20] the alternative. The data of Table III are also quite consistent with the conclusion that all desorbed free radicals undergo aqueous-phase termination (eq 8) with the rate coefficient for this (k_{ct}) obeying the relation $k_{ex} = k_{ct} \leq k_{st} \leq k_{tr}C_M$.

In principle, further information to help resolve this question could be obtained by comparing the values of the radical-loss rate coefficients obtained from these studies with those predicted from eqs 5 and 6. Unfortunately, the values obtained by the complete reentry and complete termination hypotheses only differ by a factor of 2, and not all the quantities in eqs 5 and 6 are known with sufficient precision to make a prediction to greater than this accuracy. The problems are with the values of D_{aq} and k_p^1. Although monomer diffusion coefficients in water are well-known, it can be plausibly argued that the aqueous phase in the immediate vicinity of the particle surface may contain entities which significantly slow down the diffusion of a monomeric species. More importantly, although it is likely that the propagation rate coefficient of a monomeric free radical is significantly greater than that of a macroradical, there are as yet no reliable measurements of this quantity. If we assume that k_p^1 is $2k_p$, and take $D_{aq} = 10^{-5}$ cm^2 s^{-1} (both values being plausible), one obtains from eqs 5 and 6 $k_{ex} = 5 \times 10^{-3}$ s^{-1}, which is certainly consistent with the results reported in Table III. However, while this calculation suggests that the transfer–diffusion mechanism is physically reasonable, the uncertainty in the various quantities involved precludes any further deductions being made. It is apparent however that the techniques given in the present paper can be used in more extensive experiments in a way that should lead to a resolution of the problem.

Conclusions

The work presented here has established that the addition of an appropriate aqueous-phase free-radical trap (Fremy's salt) can result in termination of all desorbed free radicals before these free radicals can enter another particle; moreover, this termination only takes place when the desorbed free radical has diffused some distance from its parent particle. The technique can be used to gather qualitative and quantitative information about the fate of desorbed free radicals in the absence of added spin trap. Observed radical-loss rates in the presence and absence of spin trap are quantitatively consistent with the transfer–diffusion model for exit. Unfortunately, the present data are insufficiently extensive to determine, for the styrene system studied here, whether *in the absence of a spin trap* the desorbed free radicals always undergo aqueous-phase termination, always reenter another particle, or whether both fates are significant. The resolution of this question for a given system is important not only for understanding growth kinetics but also because a knowledge of which mechanism(s) is (are) operative is important in unraveling the complexities of particle nucleation.[9] However, application of the techniques pioneered here and applied to a single system should prove of real use in the future to answer these questions for a wide range of systems and conditions. Means to resolve these questions for any system include carrying out FS relaxation studies as a function of particle size (to test whether k_{st} obeys eqs

5 and 6) and a function of concentrations of both FS and particles (to test whether the FS terminates the desorbed free radical before it diffuses a sufficiently large distance from its parent particle).

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Registry No. PhCH=CH$_2$, 100-42-5; Fremy's salt, 14293-70-0.