On the Apparent Effect of Nonideal Inhibition or Retardation in Emulsion Polymerization Reactions

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Emulsion polymerization initiated by γ-radiation has been used extensively by the group at the University of Sydney to study the mechanisms of emulsion polymerization reactions. Such experiments involve multiple insertions and removals of the reaction vessel into and from the γ-radiation source, thereby switching "on" and "off" the source of free radicals. The polymerization rate increases, often to a steady state value, while in the radiation source and then decays to another, lower but finite, steady state value upon removal from the source. Reinsertion of the reaction vessel once again increases the rate of polymerization. The analysis of such experiments uses the data from the approach to steady state as well as the steady state data, and therefore it is imperative that no retardation effects on the initial rate of polymerization be present; otherwise the method becomes invalid.

Such experiments utilizing γ-radiation as described above were presented in a recent paper[1] and involved the copolymerization of styrene and methyl acrylate in the presence of polystyrene latex particles, i.e., seeded polymerization. Data from two of these experiments are shown in Figure 1. The authors noted that the rate of increase of the polymerization reaction rate on the first insertion into the γ-radiation source was slower than for subsequent insertions. This was taken as evidence that species present in the reaction caused some retardation of the reaction rate and that such species were consumed during the first insertion, resulting in faster increases of reaction rates for subsequent insertions. The polymerization rate increases were then very similar between these subsequent insertions. It should be noted that the final steady state rates for all of the first and subsequent insertions were very similar.

However, visual inspection may not be sufficient to reach any conclusion with regard to possible retardation effects, as the polymerization rate immediately before insertion into the γ-radiation source must be taken into account. In the case of the first insertion, the polymerization has not commenced and thus the system is starting from a zero rate and increases to a steady state rate. Upon removal from the radiation source the reaction rate decays, not to zero, but to a finite steady state rate known as the thermal rate (see Figure 1). The approach to steady state on the second insertion will therefore be more rapid since the system is not starting from zero rate but from an appreciable rate. All the data must be analyzed to determine the polymerization rate coefficients and only then can a conclusion be drawn as to the presence of retardation effects.

Such an analysis can be carried out with the data from Schoonbrood et al.[1] The simplest analysis is that of the slope−intercept method for the zero−one system[2] in which it is assumed that bimolecular termination within a particle is essentially instantaneous and thus no more than one free radical can occupy a particle at any one time. The slope, or the rate of change of the

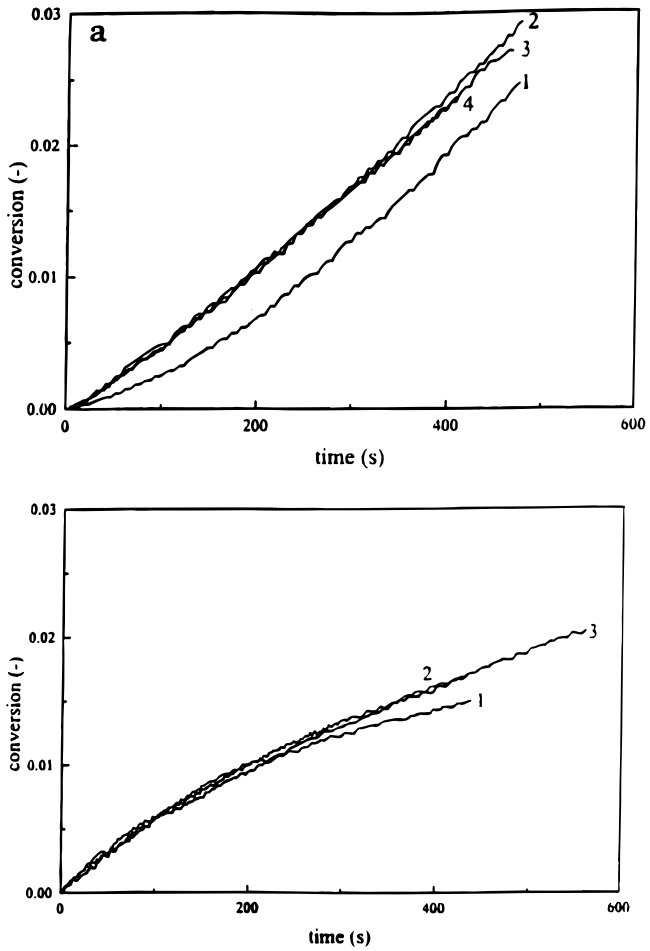

Figure 1. Conversion versus time of (a) four consecutive insertions into the γ-radiation source and (b) three consecutive relaxation runs for the copolymerization of styrene and methyl acrylate on a polystyrene seed latex. Reprinted with permission from Schoonbrood et al.[1] Copyright 1995 American Chemical Society.

fractional conversion is related to the average number of free radicals per particle, $\bar{n}$, by $R = \mathrm{d}x/\mathrm{d}t = A\bar{n}$, where x is the fractional conversion and A is a constant for the system. The analysis gives rise to the pseudo-first-order rate coefficient for entry of free radicals into a latex particle, denoted by ρ, and the rate coefficient for exit of free radicals from latex particles, k. In addition, ρ may be written as $\rho = \rho_a + \alpha k\bar{n}$, where α is the "fate parameter", a dimensionless parameter which takes into account the various kinetic events involving desorbed free radicals ($-1 \leq \alpha \leq 1$). Methods for deducing the value of ρ_a and k have been given elsewhere,[2,8] but it is important to note that the method requires the slope of the steady state rate and the intercept of the slope from a conversion versus time graph. Thus the difference in approach to steady state between the first and subsequent insertions will be seen in the value of the intercept.

It is acknowledged that the model for zero−one emulsion polymerization developed by Schoonbrood et al.[1] is much more sophisticated than the model used here, but it is considered that this model is sufficient for the purposes of this paper.

The experimental data of Schoonbrood et al.[1,11] was analyzed by the slope−intercept method.[2] Slope and intercept data for the approach to steady state in the γ-radiation source was taken from Figure 1[1] and Schoon-

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Table 1. Results from Analysis of the Data of Schoonbrood et al.[1,11]

insertion	slope (10^{-5} s^{-1})	intercept (10^{-3})	$\bar{n}_0$	$\bar{n}_f$	ρ_a (10^{-3} s^{-1})	k (10^{-3} s^{-1})
			$\alpha = 0$			
			No Correction for Polymerization Rate Prior to Insertion:			
1	6.55	−7.85	0	0.446	3.72	0.91
2	6.55	−3.85	0	0.446	7.59	1.85
3	6.32	−3.37	0	0.430	8.06	2.63
			Corrected for Finite Polymerization Rate Prior to Insertion:			
1	6.55	−7.85	0	0.446	3.72	0.91
2	6.55	−3.85	0.193	0.446	4.30	1.05
3	6.32	−3.37	0.185	0.430	4.59	1.50
			$\alpha = -1$			
			No Correction for Polymerization Rate Prior to Insertion:			
1	6.55	−7.85	0	0.446	3.99	0.77
2	6.55	−3.85	0	0.446	8.15	1.57
3	6.32	−3.37	0	0.430	8.52	2.44
			Corrected for Finite Polymerization Rate Prior to Insertion:			
1	6.55	−7.85	0	0.446	3.99	0.77
2	6.55	−3.85	0.193	0.446	4.75	0.91
3	6.32	−3.37	0.185	0.430	4.97	1.42

brood,[11] along with the polymerization rates after removal from the γ-radiation source. Thus, for insertion 1, the initial value of $\bar{n}$, $\bar{n}_0$, was zero and the final value of $\bar{n}$, $\bar{n}_f$, was derived from the steady state polymerization rate. However, for insertion 2, $\bar{n}_0$ was obtained from the steady state polymerization rate of relaxation 1. Similarly, $\bar{n}_0$ for insertion 3 was obtained from the polymerization rate of relaxation 2. Insertion 4 was sufficiently close to insertion 3 as to be considered identical. Of the parameters needed to calculate the constant A, the average propagation rate coefficient, k_p, and the monomer concentration within the latex particles, C_m, were 303 dm^3 mol^{-1} s^{-1} and 5.8 mol dm^{-3}, respectively, the number of seed latex particles in the reactor was 5.19×10^{15}, and the amount of monomer was 10.05 g,[1,11] sufficient to keep the system in interval II, *i.e.*, in the presence of monomer droplets, for the period under consideration.

Table 1 gives the results of the analysis assuming the fate parameter, $\alpha = 0$. The average number of radicals per particle, $\bar{n}$, was less than 0.5, and thus the use of the zero−one model is valid. In the first analysis the initial rates for all of insertions 1−3 are considered to be zero and it can be seen that the value of ρ_a increases significantly from the first to the second insertion, with the value derived from the third insertion similar to that from the second. However, if the analyses for insertions 2 and 3 are corrected for the initial polymerization rates, i.e., the polymerization rates to which the system relaxed upon removal from the source, then the values of ρ_a are consistent for all of the three cases and are within experimental error. It is also important to note that the values of k differ markedly between all three runs when no correction is made for the initial rate. The exit rate parameter should be independent of aqueous phase events, yet it is clear that there is a difference between all three insertions when no correction for initial rate is made. In contrast, the values for k are remarkably consistent when the initial rates of polymerization for insertions 2 and 3 are included in the analysis.

The same analysis was carried out for the case when $\alpha = -1$, the value of α often used for the cases of high radical flux such as a γ-radiolysis source,[2] also shown in Table 1. The same features noted for the case with $\alpha = 0$ are also present for the case when $\alpha = -1$.

From the results listed in Table 1 it is not possible to conclude that there is a retardation effect in the first insertion. Once the initial polymerization rates are taken into account for insertions 2 and 3, the resulting rate coefficients are within experimental error and thus the conclusion must be that there are no measurable retardation effects in this system, contrary to the conclusion of Schoonbrood et al.[1]

It has been stated elsewhere that "retardation effects" of this nature have been seen for methyl methacrylate and acrylonitrile, but not for styrene, butyl acrylate, and butyl methacrylate.[3] The former cases suffer from the same deficiency as in Schoonbrood et al.[1] in that only a visual inspection of the data was made.[4,5] In fact, no specific reference is made to differing approaches to steady state for the case of methyl methacrylate,[5] it is merely supposed that inhibitor was present and that it was burnt out on the first insertion. The latter cases are different in that it has been claimed that no inhibition effects are observed.[3] For butyl acrylate,[6] the multiple insertion technique was indeed used and the rates were found to be similar, hence the conclusion, but in this case the polymerization rate is so fast, e.g. > 5% conversion in 2 min, that any small effect of retardation on the initial polymerization rate would be masked by the extremely rapid rate of polymerization. No mention was made of inhibitor or retardation effects for the case of butyl methacrylate.[7] The two references to styrene polymerization[8,9] do not show multiple insertion data either. This author assumes (and concurs) that the agreement between the rate coefficients obtained from two different methods, that of initiation by potassium persulfate and γ-radiation, is the basis for the conclusion.

Table 2. Experimental Entry and Exit Rate Coefficients for Styrene Emulsion Polymerization Obtained from Multiple Insertions into the γ-Radiation Source (Data Taken from Adams[10])

	1st insertion	2nd insertion	3rd insertion	4th insertion
R_0 (10^{-5} s^{-1})	0	2.1	1.9	2.2
R_f (10^{-5} s^{-1})	3.5	3.5	3.4	3.4
$\bar{n}_0$	0	0.26	0.24	0.28
$\bar{n}_f$	0.44	0.44	0.43	0.43
intercept (10^{-3})	−2.2	−1.5	−1.1	−1.2
k (10^{-3} s^{-1})	1.8	1.1	2.0	1.4
ρ_a (10^{-3} s^{-1})	7.6	4.6	6.4	4.8

However, similar multiple insertion experiments have been done with styrene polymerization and the results reproduced in Table 2.[10] These results were obtained using the method of Whang et al.[2] with $\alpha = -1$ and accounting for the polymerization rate immediately prior to each insertion, i.e. zero for insertion 1 and a finite rate for the subsequent insertions, as shown in Table 2. The values for k are consistent within this experiment and moreover agree with those obtained by Hawkett et al.[8] and Lansdowne et al.[9] on very similar systems. The ρ_a values show significant scatter, with the ρ_a value for the first insertion actually the largest in magnitude. A brief glance at these results might imply that each insertion exhibited a rate of approach to steady state that was in proportion to the ρ_a value. However, reconstruction of the experimental data from the information in Table 2 clearly shows that the first insertion was slower to reach steady state than the subsequent insertions which were then equivalent

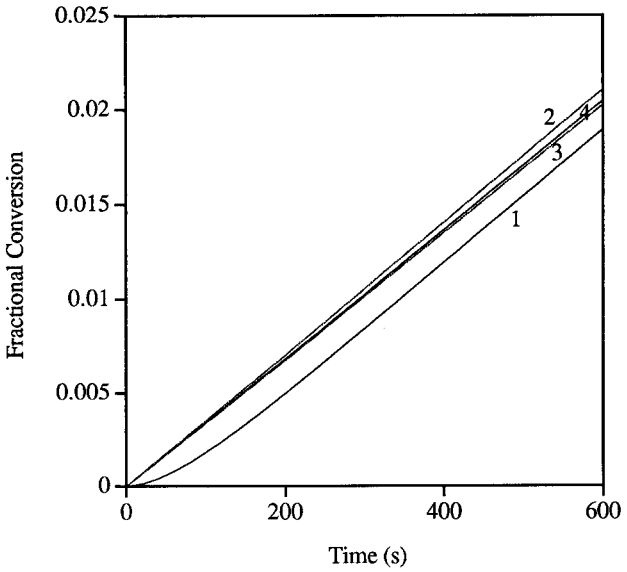

Figure 2. Reconstruction of the experimental data from Adams[10] of the γ-radiation-initiated seeded emulsion polymerization of styrene, showing that the approach to steady state of the first insertion is slower than the subsequent insertions.

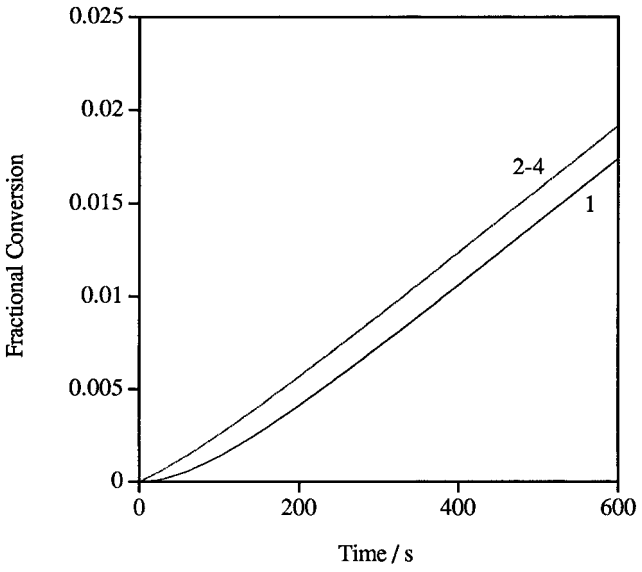

Figure 3. Simulation of styrene emulsion polymerization initiated by γ-radiation, demonstrating the difference between the first insertion, for which the initial rate equals zero with $\bar{n}_0 = 0$, and insertions 2−4 which start from a finite polymerization rate with $\bar{n}_0 = 0.25$. In all cases $\bar{n}_f = 0.45$, $\rho_a = 5 \times 10^{-3}$ s^{-1} and $k = 1.5 \times 10^{-3}$ s^{-1}, $\alpha = -1$, and $A = 8 \times 10^{-5}$ s^{-1}.

(Figure 2). These results once again demonstrate the importance of including the rate of polymerization immediately prior to insertion into the γ-radiation source in the analysis.

This effect can be easily simulated for styrene emulsion polymerization using rate parameters that are constant for each insertion, rather than the above experimentally derived parameters. The parameters used are consistent with results obtained by several authors for similar styrene emulsion polymerization reactions using a seed latex particle size of approximately 50 nm unswollen radius.[8−10] The results of the simulation (Figure 3), using the method of Whang et al.,[2] are in accord with the experimental results of Figures 1 and 2 and once again demonstrate the importance of the effect of the initial polymerization rate on the approach to steady state for the first and subsequent insertions into the γ-radiation source.

The possibility of the presence of a retardation effect in emulsion polymerization reactions is indeed a valid concern. However, the simple visual observation of differing initial polymerization reaction rates between first and subsequent insertions of the reaction vessel into a γ-radiation source cannot be used as evidence for the existence of such an effect. It has been demonstrated in this paper that the difference between the first and subsequent polymerization rates in many monomer systems can be accounted for simply by the difference between the initial zero polymerization rate at the beginning of the first insertion and the non-zero polymerization rates at the beginning of all subsequent insertions. The need to invoke the more complicated kinetic processes of retardation by a nonideal inhibitor is not required.

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