Chain-Length Dependence in Living/Controlled Free-Radical Polymerizations: Physical Manifestation and Monte Carlo Simulation of Reversible Transfer Agents

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ABSTRACT: A Monte Carlo model is used to show that chain-length dependent termination plays an important role in free-radical polymerization systems containing reversible transfer agents (RTAs) such as RAFT agents and alkyl halides. As dormant chains are activated through the reversible transfer reaction, the chain-length of the active species changes. By changing the length of the propagating radical, the RTA changes the behavior of the entire system, through the chain-length dependent termination reaction. The amount of polymer that may be produced before two radicals terminate is studied as a function of system parameters such as the transfer constant of the RTA, the concentration of the RTA, and the length of the dormant chains by modeling RTA-mediated polymerization, with emphasis on emulsion polymerizations. High transfer constant RTAs and short dormant chains exhibit significantly shorter radical lifetimes and hence have a slower overall rate of polymerization (seen as a lower average number of radicals per particle) than systems without RTA. Conversely, long dormant chains may lead to an extension of radical lifetimes and an increase in the number of radicals per particle. These effects are due to the change in the chain length of the polymeric radical because of transfer to dormant species, such that significant amounts of short−short termination are seen at low conversions and long−long termination is required at high conversions. This work also suggests several experimental techniques, including the use of oligomeric adducts to the RTA, that may offer solutions to the known problems of RTA systems in bulk, solution, and particularly emulsion polymerization.

Introduction

Living polymerization techniques have recently provided unprecedented control over the molecular weight distribution[1,2] and molecular architecture[3] using anionic polymerization[4] and various free-radical techniques including nitroxide-mediated polymerization,[5] atom-transfer radical polymerization,[6,7] alkyl halide mediated polymerization,[8,9] and more recently reversible addition-fragmentation chain transfer (RAFT).[2,10] The different living polymerization techniques are typically categorized by their basic kinetic schema. Of interest in this work are the techniques that follow reversible transfer (or degenerative transfer) kinetics, using reversible transfer agents (RTAs) such as alkyl halides and RAFT agents.

Although early studies were not overly promising, emulsion polymerization offers significant benefits to living polymerization systems.[11] On the basis of the behavior of nonliving systems, emulsion polymerization should offer faster rates of polymerization while maintaining good temperature control, negligible change in viscosity with conversion, and the technique would have the various environmental advantages of emulsion polymerization compared to solution systems.[11,12] The study reported here makes use of emulsion polymerization as a model of solution and bulk reactions at a small scale, offering the opportunity of simulating small volumes of reaction mixture as well as working toward improvement of the problems exhibited by RTA/emulsion systems. The additional physical aspects introduced by the heterogeneous polymerization system (such as radical entry into particles and compartmentalization of radicals) change the relative importance of different reactions in the RTA-mediated polymerization. In particular, the importance of chain-length dependent reactions becomes easier to study in the model system, although the conclusions are also applicable to bulk and solution systems.

Living polymerization techniques are now well developed for solution and bulk polymerization systems; however, relatively few examples of living polymerization in emulsion polymerization have been reported where good colloidal stability has been maintained throughout, reasonable reaction rates have been observed, and good molecular weight polydispersity has been measured. Butté et al.[13] concluded from a study of the reaction pathways and water solubility of the species involved in various living polymerization techniques that (of the living polymerization techniques available at the time) reversible transfer was most likely to work in emulsion systems. Loss of deactivating species (such as the transition-metal complexes used in ATRP or the stable nitroxide radical) through desorption from the particles was their primary concern; this process is preventable in reversible transfer systems as the deactivating species is part of a long polymeric chain and hence may be kept within the particle. Butté et al.[13] further postulated that the transport of the RAFT agent to the locus of polymerization (i.e., the particle) would be problematic in emulsion polymerization systems and sought to obviate the need for this by employing miniemulsions.

Few results have been reported for the use of alkyl iodides in emulsion polymerization, the work of Lansalot et al.[14] and Butté et al.[13] illustrating the difficulties of

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this area. The results from these studies supported the conclusions of Butté et al.[13] regarding the transport of the alkyl halide to the particles.

Some advances in true emulsion polymerization with RAFT were made with low transfer constant xanthates[15,16] and high transfer constant dithioester RAFT agents.[17] More recently, work by Prescott et al.[18] in seeded emulsion polymerization and Ferguson et al.[19] in ab initio systems has illustrated a pathway to successful implementation of RAFT in emulsion polymerization by explicitly designing the systems such that transport of the RAFT agent to the particles is not needed during the polymerization step.

Remaining unexplained is the reduction in the rate of polymerization seen in many reactions, including bulk, solution, emulsion, and miniemulsion systems in which good molecular weight control is seen.[2,11] The origins of this reduction in rate have recently received considerable attention; theories including the slow fragmentation of the intermediate bipolymeric radical,[20−22] irreversible[23] and reversible[3,24] termination of the intermediate radical have been espoused. It has been noted,[22] however, that benzyl activated RAFT agents such as the one used by Prescott et al.[18] and the trithiocarbonates used by Ferguson et al.[19] have a much less stable intermediate radical. On this basis, it is not expected that the intermediate radicals formed by these RAFT agents would have the problem of slow fragmentation. Hence, they would not undergo significant amounts of intermediate radical termination, as the intermediate radical concentration is much lower.

The search for a mechanism for the reduction in the rate of polymerization observed in RTA-mediated systems is still underway. One of the key differences between a classical polymerization and an RTA-mediated system is the chain length of the reacting polymeric radicals. The diffusion of the propagating radical has been shown, through both theoretical arguments[25,26] and recent experiments,[27,28] to be important in controlling the termination reaction. Recent work by Vana et al.[29] illustrated how CLD termination rate coefficients could be obtained in the limit of dilute solution, indicating that the effects of CLD termination are evident in macroscopic quantities such as the rate of polymerization of the system; here, it is shown that CLD termination is crucial to understanding of RTA-mediated polymerizations and may not be omitted, making the results presented by other modeling efforts that do not use CLD kinetics[21,30] considerably harder to interpret.

The importance of CLD termination reactions is well illustrated in the kinetics of particle growth in an emulsion polymerization. The applicability of various kinetic models to the growth of emulsion polymerization particles containing RTA has been discussed elsewhere, with the difficulties involved evident in previously published discussions (see, for example, Monteiro et al.[17] and Prescott et al.[11]). The use of conventional kinetic schemes such as "zero-one" or "pseudo-bulk" (both discussed below) allows rate coefficients to be obtained from experimental data with a minimum of model-based assumptions,[12] and these techniques have been recently applied to various RTA-containing systems.[15,17] Here, the appropriateness of these treatments is investigated.

In this work, the influence of CLD processes in normal emulsion systems is first examined, followed by the influence of RTAs. From these investigations, the applicability of the zero-one and pseudo-bulk limits will be examined. Moreover, the reduction in the rate of polymerization because of the addition of the RTA and the acceleration in reaction rate that occurs throughout the reaction will be explored with reference to CLD termination. On the basis of the conclusions drawn from the study of RTA/emulsion systems, similar conclusions for RTA-mediated solution and bulk polymerizations may also be drawn.

Free-Radical Polymerization in Confined Systems: Particle Growth Kinetics. One of the models that has been successfully adopted to describe free-radical polymerization in confined systems, especially emulsion polymerizations, is where the kinetics of particle growth are categorized by the limit where the entry of a second radical into a particle leads to "pseudo-instantaneous" termination.[12,31,32] There may only ever be zero or one radical in a particle following this model (two radicals always terminate immediately); hence, it is usually termed "zero-one kinetics". This is a useful mathematical limit that is accurately applicable to many systems.[12] Indeed, both the zero-one and pseudo-bulk limits for particle growth have provided useful tools for obtaining rate coefficients from experimental data with a minimum of model-based assumptions.

Determining the applicability of zero-one kinetics to a system requires formalizing the meaning of "pseudo-instantaneous" along with additional information about the study being performed. In practice, for many emulsion polymerization systems (such as those with styrene particles with a swollen radius less than about 60 nm) termination between two radicals is so fast as to allow this mathematical simplification to be successfully made.[12,32]

The original definition of a zero-one system incorporated instantaneous termination between two radicals in the same particle.[12,31,32] In the rigorous derivation of zero-one kinetics presented by Casey et al.[31] and Gilbert,[12] sufficient and necessary conditions for a system to be zero-one were developed. Within the mathematical framework developed by Casey et al.[31] and Gilbert,[12] a condition for the applicability of zero-one kinetics that is both sufficient and necessary is that $c^{SL} \gg k_pC_p$ where c^{SL} is the pseudo-first-order rate coefficient for termination between a short chain and a long chain, k_p is the propagation rate coefficient, and C_p is the monomer concentration in the particle. On this basis, it is possible to establish whether zero-one kinetics are appropriate to a system without reference to the rate of radical entry in the particles.

Following advances in the understanding of CLD termination,[26,33] Maeder and Gilbert[34] were able to relax the above condition somewhat, requiring instead that termination should occur before a significant amount of polymer had been made. Moreover, using CLD termination rate coefficients, they calculated the probability that an entering radical would propagate to various lengths before termination had occurred, showing how this related to the zero-one idea of pseudo-instantaneous termination. Plots showing the amount of polymer made (in terms of the degree of polymerization of the entering species) have now been successfully used to evaluate the "zero-one-ness" of particles in various different studies.[35]

The meaning of "significant amount of polymer" is dependent on the problem under consideration. For example, when seeking to obtain kinetic parameters for radical entry and exit from a γ-radiolysis experiment

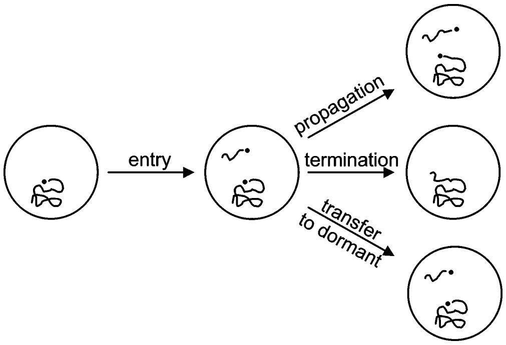


Figure 1. Schematic representation of the situation modeled in this study. The radicals may propagate or transfer to a dormant species or undergo a chain-length dependent termination reaction (by combination or disproportionation). The only effect of the transfer to dormant species reaction is to change the length of the propagating radical, as discussed in detail here.

on a system to which “Limit 2b” kinetics apply (i.e., continual re-escape of monomeric radicals[12]), “pseudo-instantaneous termination” may be rephrased as the requirement that a monomeric radical entering a particle containing another radical terminate with that radical before it has the opportunity to desorb once more.[12]

Upon further consideration of the work of Maeder and Gilbert,[34] several useful extensions for living radical polymerization were identified, along with an inconsistency that may be readily corrected. (The corrected derivation is given in the Appendix. It is also shown in the Appendix that in the corrected calculations, the butyl acrylate system used by Maeder and Gilbert[34] is not zero-one as was first believed. However, it is concluded that the primary chain-stopping event is still transfer to monomer; hence, the values for the second-order rate coefficient for transfer to monomer in butyl acrylate are no less accurate for this omission.)

Chain-Length Dependent Reactions. The CLD termination reaction has been the topic of considerable research.[26] In interpreting the modeling results presented here, the concepts of “short” and “long” will be used. While any chain length used as a cutoff between these descriptors would obviously be an artificial distinction, the systems under consideration here are generally involving quite short chains (dp of 10 or less) or long chains (dp of 100 or more). The essence of the CLD effects in the systems under consideration here may be captured by looking at the three combinations: short−short, short−long, and long−long; however, the detailed accounting of all chain lengths is required for the modeling process.

Theoretical Section

Mechanisms Under Consideration. The physical system modeled in this study is shown in Figure 1. Taking the behavior of the radicals in an emulsion polymerization particle as an example of the behavior of homogeneous polymerization, a particle with a preexisting radical has a new radical enter it from the aqueous phase. These two radicals may then either propagate or terminate, or in the presence of an RTA, transfer radical activity to a dormant chain. The number of propagation steps that take place inside this particle before termination occurs gives an indication of the validity of zero-one kinetics.

The reactions that a polymer chain i-units in length, P_i, may undertake are thus

$$P_i^\bullet + M \xrightarrow{k_p} P_{i+1}^\bullet \tag{1}$$

$$P_i^\bullet + P_j^\bullet \xrightarrow{k_t^{ij}} P_{i+j} \text{ or } P_i + P_j \tag{2}$$

$$P_i^\bullet + D_k \xrightarrow{k_{tr,D}} D_i + P_k^\bullet \tag{3}$$

where k_t^{ij} is the second-order rate coefficient for the CLD termination of an i-meric chain with a j-meric chain and $k_{tr,D}$ is the rate coefficient for transfer of radical activity from the radical $P_i^\bullet$ to the dormant chain D_k.

It may be noted that none of these reactions is specific to an emulsion polymerization system and that each of eqs 1−3 will occur in bulk or solution polymerization (up to the effect of solvents on the rate coefficients of the processes). It is only the compartmentalization of radicals into the particles that makes this model emulsion polymerization-specific, at the same time making it also computationally simpler as only two radicals need to be considered at any stage. The conclusions from this work are thus applicable not only to emulsion polymerizations containing an RTA, but also to RTA-mediated bulk and solution polymerizations and potentially also to other living radical polymerization techniques.

Choice of Modeling Approach. The addition of an RTA further complicates the analytic method presented by Maeder and Gilbert.[34] If chain-length *independent* termination were used, then the standard evolution equations for the populations of dormant, active, and dead chains could be trivially solved; however, once CLD termination is included, the lengths of not only the active species but also all the dormant species must be included in the evolution equations. Moreover, the length of the propagating radical is able to change not only through propagation but also via the transfer to dormant reaction.

A natural alternative to the analytic approach of Maeder and Gilbert[34] is to continue with the probabilistic calculations, embodying them within a Monte Carlo simulation. This way, each event step may include both transfer to dormant species (and the associated change in the length of the propagating radical) and CLD termination.

Monte Carlo Model. The basic principle behind the Monte Carlo model used here is to consider in turn each radical and calculate the probability that it will follow each of reaction pathways open to it (eqs 1−3). A pseudo-random number is used to select which of the possible events occurred. The products of this reaction are then considered for further reaction (eqs 1−3) until termination takes place. As discussed in more detail later, the number of propagation steps undertaken by the two radicals before they terminate is used as a measure of the lifetime of the radicals in the particle.

The Monte Carlo model developed for this study makes use of recent advances in pseudo-random number generators and time-dependent Monte Carlo modeling.

Monte Carlo Probabilities. As with the model of Maeder and Gilbert,[34] pseudo-first-order rate coefficients may be used to calculate the probabilities that each of eqs 1−3 is followed. The pseudo-first-order rate coefficient for propagation of a radical $P_i^\bullet$ is k_pC_p (where C_p is the concentration of monomer in the particle) and the pseudo-first-order termination rate for the reaction

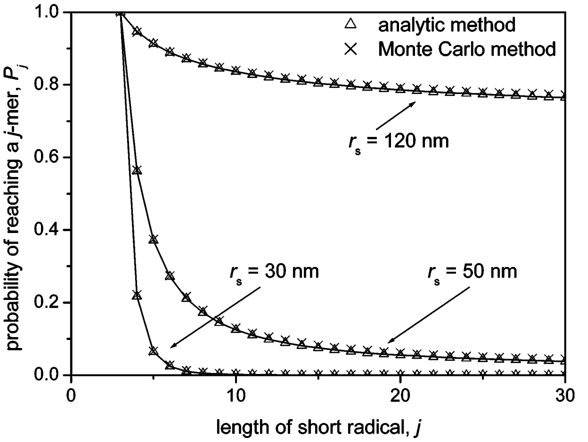


Figure 2. Comparison between the analytic method (based on the work of Maeder and Gilbert[34]) and the Monte Carlo techniques described herein, for a variety of swollen radii r_s. Note that in all figures, the lines between points are a guide to the eye only.

between a $P_i^•$ and a $P_j^•$ (where there is only one $P_j^•$ in the particle) is determined by the swollen radius of the particle, r_s, and given by k_t^{ij}/N_AV_s. The pseudo-first-order rate coefficient for the transfer to D_k species is thus $k_{tr,D}n_k^D/N_AV_s$, where n_k^D is the number of D_k species in the particle (typically the total number of dormant species is 10^2-10^5 per particle). For a particle containing one $P_i^•$, one $P_j^•$, and a number of D_k (indeed, a distribution of D_k), the probability, *P*, of each of the three classes of events occurring (noting that eq 6 is true for each of the D_k molecules present) is thus

$$P(P_i^• + M) = \frac{k_p{}^iC_p}{\Delta_i} \qquad (4)$$

$$P(P_i^• + P_j^•) = \frac{k_t{}^{ij}/N_AV_s}{\Delta_i} \qquad (5)$$

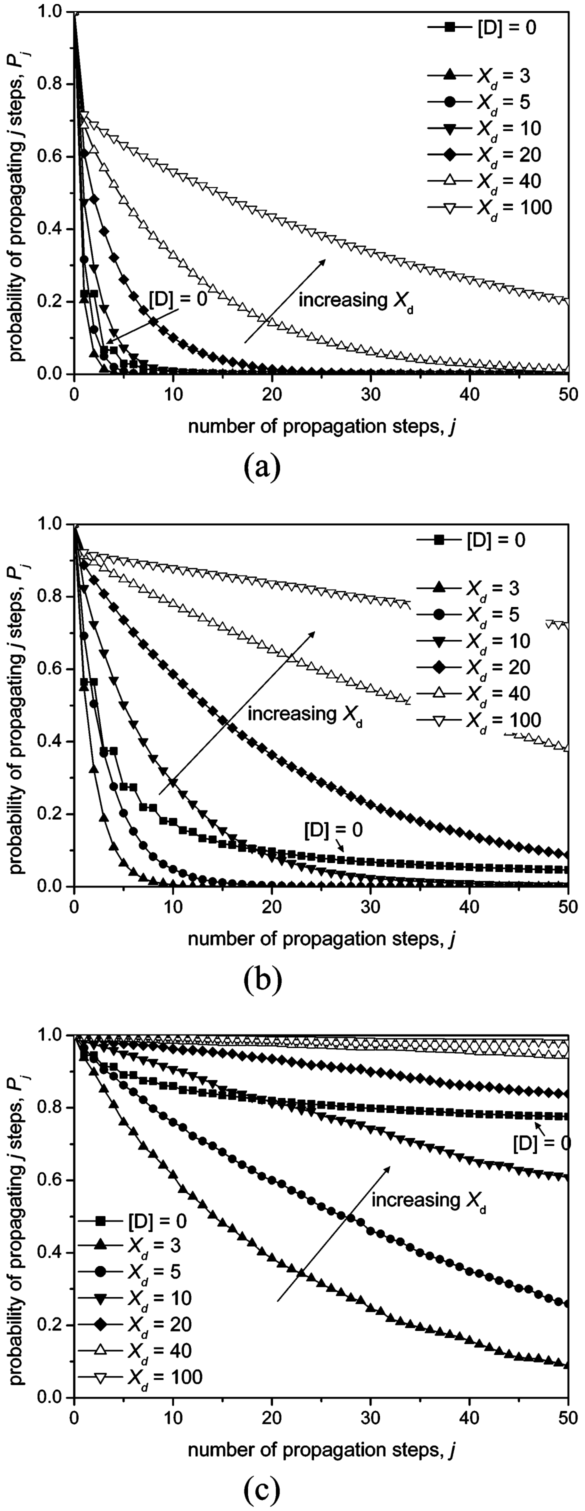
$$P(P_i^• + D_k) = \frac{k_{tr,D}n_k{}^D/N_AV_s}{\Delta_i} \qquad (6)$$

where Δ_i is the CLD sum of all events:

$$\Delta_i = k_p{}^iC_p + \frac{k_t{}^{ij}}{N_AV_s} + \sum_k \frac{k_{tr,D}n_k{}^D}{N_AV_s} \qquad (7)$$

Adaptation of Analytic Step Counting. In the analytic case presented by Maeder and Gilbert for the absence of the RTA, the use of the length of the radical, *j*, as a measure of the amount of polymer produced is a natural choice (see, for example, Figure 2).[34] In the case of a system where RTA is present, however, it is no longer possible to use the length of the radical as the measure of the amount of polymerization that has taken place as the radical activity is passed between many chains of different lengths.

For this reason, the use of the number of propagation steps undertaken (or equivalently the number of monomer units consumed) becomes a better measure. As both the preexisting radical and the entering radical may undergo both propagation and transfer to dormant species, the number of propagation steps of both radicals must be counted. The effect of this is to stretch this measure by a factor of 2 (for the two radicals) as is seen in the figures shown in the Results section.



(a)

(b)

(c)

Figure 3. Probability of radicals surviving at least *j* propagation steps without termination—the influence of X_d on the ability to have more than one radical in the particle for a range of particle sizes with the high-activity RTA C_{tr} = 6000 at [D] = 8.5 mM. The number of propagation steps, *j*, is a measure of the number of monomer units consumed, while the probability of propagating at least *j* steps is denoted P_j. (a) r_s = 30 nm, (b) r_s = 50 nm, (c) r_s = 120 nm. Note that a and b follow zero-one kinetics in the absence of an RTA.

The reader may also wish to consider the following alternative axis title for Figure 3−5: the "probability of propagating at least *j* steps" may also be thought of as the “probability of consuming at least j monomer units before termination occurs”.

Time Coordinate. The time-dependent Monte Carlo simulation used in this study requires a measure of time to be associated with each step. Following the method of Fichthorn and Weinberg,[36] the time-step, τ, for the reaction event of a $P_i^\bullet$ is given by

$$\tau = -\frac{\ln(U_2)}{\Delta_i} \tag{8}$$

where U_2 is a uniform deviate on [0,1] (note that U_2 is not the same number as was used to choose which event occurred). Each reacting species in the system is given its own time coordinate, with only species existing at the same time (to within a small error, discussed below) being permitted to react.

This approach is equivalent for systems that are sufficiently large or over a sufficiently long time.[36,37] In the two radical systems presented here, the former condition is not met; however, the latter condition is met within a few steps. A further analysis of the suitability of this time-dependent method may be found in the Results section.

Random Source. Uniform deviates on the interval [0,1] were obtained using the random bits contained in the Marsaglia Random Number CDROM.[38] The random bitstream was first converted into a series of eight-byte, unsigned integers and then divided by the maximum such integer to give an approximately 15 significant figure real number on [0,1]. The bitstream on the CD was developed by Marsaglia[38] for use in Monte Carlo calculations and is the combined output of various physical sources of white noise along with other pseudorandom number generators such as the multiply with carry generator which is used in the Monty Python method for generating random variables.[39]

Calculation of Rate Coefficients. While the values of k_p and $k_{tr,D}$ have experimentally determined values that may be readily used in the simulations described here, k_t^{ij} must be calculated on the basis of models reported elsewhere. In the work presented here, k_t^{ij} is assumed to take the generalized form described by Russell et al.,[40] with dependence on both i and j. Specifically, k_t^{ij} is a function of the mutual diffusion rate coefficient D^{ij}:

$$k_t^{ij} = 4\pi D^{ij} p^{ij} \sigma N_A \tag{9}$$

where p^{ij} is the probability that the two radicals will undergo termination when within a capture distance σ. The parameter p^{ij} accounts for the need for the two radicals to have opposite spin to undergo termination and is usually taken to be 1/4, except in glassy systems.[41,42] It has been argued[40] that D^{ij} may be given by

$$D^{ij} = D_i^{com} + D_j^{com} + 2D^{rd} \tag{10}$$

Expressions for the center-of-mass diffusion coefficient, D_i^{com}, and the reaction−diffusion coefficient, D^{rd}, may be derived from the work of Scheren et al.,[33] Griffiths et al.,[43] and Russell et al.,[40] as described in the Appendix.

Model Implementation

A variety of numerical experiments were performed to explore the effect of a reversible transfer agent on the kinetics of particle growth. In particular, the effects of variation in the degree of polymerization of the dormant species, X_d, the swollen radius of the particles, r_s, the concentration of the dormant species, [D], and the chain transfer constant, C_{tr}, were studied. Additional numerical experiments were performed to show that the Monte Carlo approach used here was equivalent to the analytic approach previously described,[34] at least in the absence of RTA.

Table 1. Parameters Varied between Numerical Experiments

parameter	range
[D]/mmol dm^{-3}	3−20
r_s/nm	30−120
X_d	3−100
C_{tr}	0.5−6000

Table 2. The Values of C_{tr} Used in This Study along with RTAs that Have Those Values for C_{tr}

C_{tr}	RTA equivalent
0.5	PSt−SCSOEt (Adamy et al.[b])
200	PSt−SCSCH$_3$ (Goto et al.[c])
6000	PSt−SCSPh (Goto et al.[c])[a]

[a] Obtained at 40 °C. [b] Reference 47. [c] Reference 48.

Although the propagation rate coefficient, k_p, will have a significant role in the particle kinetics, a single illustrative system was chosen for demonstrating the importance of CLD kinetics in living polymerizations. The emulsion polymerization of styrene at 50 °C with a persulfate initiator has been widely studied by many groups and has been shown to exhibit zero-one kinetics for small particles[44,45] and pseudo-bulk kinetics for larger particles.[12,46] The addition of an RTA may thus have interesting effects on the kinetics of both large and small particles. Moreover, this system is one for which rate of polymerization versus time data have been obtained in the presence of several different RTAs, including a high-activity RAFT agent[18] and low-activity xanthate-based RAFT agents.[15] The widespread study of the bulk (and emulsion) polymerization of styrene with various RTAs also provides values for C_{tr}, allowing direct comparison between these models and physical systems.

The range of values for X_d, r_s, [D], and C_{tr} used in these numerical experiments are shown in Table 1. The specific values of C_{tr} used are shown in Table 2 along with the corresponding real RTAs (e.g., xanthates and dithioesters) to which they correspond. The values of [D] used in this study are over the range reasonably used in emulsion polymerization,[17−19] giving molecular weights (at 100% conversion) of between 3×10^4 and 2×10^5 in the model system.

The diffusion calculations were undertaken using the parameters for monomer diffusion of Scheren et al.,[33] with other parameters from Russell et al.[49] (interaction radius $\sigma = 0.7$ nm; step length for reaction diffusion $a = 0.6$ nm) and the scaling law for the chain length and w_p dependence from Griffiths et al.,[43] as discussed in the Appendix. The scaling law of Griffiths et al.[43] was originally developed only for species up to decamer length but over a variety of w_p, including those typically used in emulsion polymerization (i.e., $w_p \gtrsim 0.4$) hence use in this situation is somewhat of an extrapolation of the model. Other work on CLD termination (e.g., that of de Kock et al.[28] and Smith et al.[50]) has been confined to dilute solution and also requires significant extrapolation to permit use in this model. While this situation

Table 3. Parameters Used in the Numerical Experiments that Are Specific to the Model System under Consideration (Styrene at 50 °C with Persulfate Initiator)

parameter	value	ref
C_p/mol dm^{-3}	5.5	12
w_p	0.39	*a*
k_p/dm^3 mol^{-1} s^{-1}	236	57
z	3	12, 52

[a] The w_p of the model system in Interval II emulsion polymerization (i.e., in the presence of aqueous monomer droplets).[12]

may seem discouraging, the nature of the Monte Carlo model is that it compares the rates of the processes involved and is relatively insensitive to the actual values involved. Moreover, the treatment presented here is rather qualitative and the conclusions are not changed even by (say) a doubling of ($\langle k_t \rangle$) as would be suggested by the difference between the model used here and that of de Kock et al.[28]

Additional parameters tied closely to the model system investigated are given in Table 3. The length of the entering radical, *z*, is included here, on the basis of the Maxwell−Morrison model for entry.[51,52] In this model, the entering species is a *z*-meric radical where *z* is the critical degree of polymerization for the oligoradical to become surface active. This model has been quite successful in describing various experimental systems.[53−56] For hydrophobic monomers with a charged initiator end group, *z* is quite small, for example, styrene with a persulfate initiator has $z = 2$ or 3.[52,53]

The only simulation parameter required for the time-dependent Monte Carlo simulation is δt_{max}, the maximum time range in which objects may be considered to be simultaneous in the simulation. The chosen value for δt_{max} (0.002 s) was approximately $2/(k_pC_p)$ where $1/(k_pC_p)$ is the time taken for the most common event step. The number of particles considered (starting each time at the beginning of Figure 1) was 10^5 for most of the systems reported here, with 10^4 particles being used for some of the more numerically intensive systems. Sensitivity to both the number of particles considered and δt_{max} was assessed, indicating that these choices were appropriate.

The simulations were performed over a distributed computing grid at CSIRO Molecular Science that was developed for this study. Simulation times varied from seconds to days, with the number of dormant species in the particle being a primary factor in determining the simulation time.

Results

Varying X_d, r_s, [D], and C_{tr} (each giving a set of P_j vs *j* values) provides a complex parameter space to analyze. Here, the specific effects of each of these parameters will be addressed in turn to build a coherent picture of the influence of RTAs first on emulsion polymerization systems and then on RTA-mediated polymerization in general.

Consistency with Analytic Solutions. In the absence of dormant chains, it is possible to obtain analytic solutions for the probability of propagating to various lengths, as presented by Maeder and Gilbert.[34] Such probability curves are presented in Figure 2, where the probability of obtaining a chain *at least j* units long is given by P_j. In Figure 2, the entering radical (*z*-mer) is already three units long, so $P_3 = 1$. From Figure 2 it is possible to conclude that small particles (such as r_s = 30 nm) are unable to support more than one radical in the particle with termination between the short entering radical and the preexisting radical being rapid (within a few propagation steps), hence "zero-one" kinetics are appropriate. In large particles (such as r_s = 120 nm), the likelihood of termination is much less and each particle may contain more than one radical for a considerable period of time, hence "pseudo-bulk" kinetics is a more apt description. The applicability of zero-one kinetics may thus be determined from these plots.

Importantly, the Monte Carlo model developed in this study gives the same results (both qualitatively and quantitatively) as the analytic solution, as shown in Figure 2. This is a necessary condition for the validation of the model, indicating that the adaptive time-step technique gives the same results as the analytic solution when counting the length of the entering radical.

Note that subsequent figures use the number of propagation steps since entry occurred rather than the length of the radical, as noted above in Adaptation of Analytic Step Counting. While the adaptive time-step approach exhibits some unphysical lack of smoothness at early steps (see, for example, [D] = 0 in Figure 3), the correspondence between the analytic and Monte Carlo results shown in Figure 2 is important evidence in establishing its accuracy.

Influence of Dormant Chain Length. For high-activity RTAs (with $C_{tr} \gg 1$), the length of the dormant chains in a particle is a function of the amount of RTA added to the particle and the amount of monomer converted to polymer in the particle. For low-activity RAFT agents, however, the average length of the dormant chain remains fairly constant throughout the reaction (unless the target $\bar{M}_n$ is particularly small), being about that of the target $\bar{M}_n$.[47,58] This is seen in numerous simulations and experiments with low-activity xanthates, as has been discussed by Adamy et al.[47] and Monteiro and de Barbeyrac.[58] Consequently, the dormant chain length will have little effect in real systems using low-activity RTAs and this section will be confined to the high-activity RTA listed in Table 2.

In a particle containing a high-activity RTA, the dormant chains are quite short at low conversions and then significantly longer in the later stages of the reaction. The nature of CLD effects would thus be expected to vary during the course of the reaction. Figure 3 shows that at low conversions, when the dormant chains are quite small, the effect of the RTA is to reduce the ability for the test particle to contain more than one radical. This means that the zero-one limit is more applicable to the particles at low conversions in the presence of RTA than in its absence. Equally, the zero-one limit is less applicable at higher conversions, with the particles having a greater propensity to hold two radicals within them without termination occurring. In each case shown in Figure 3, short dormant chains lead to more rapid termination than in the absence of the RTA (shown for reference on each plot as [D] = 0) and longer chains lead to much slower termination.

Moreover, Figure 3 indicates that even RTA-containing particles as large as r_s = 120 nm may be treated as being zero-one at low conversions. Thereafter, they return to a situation whereby two (or possibly more) radicals may be successfully contained within them with little chance of termination within the time scale of a significant amount of polymer being produced. This

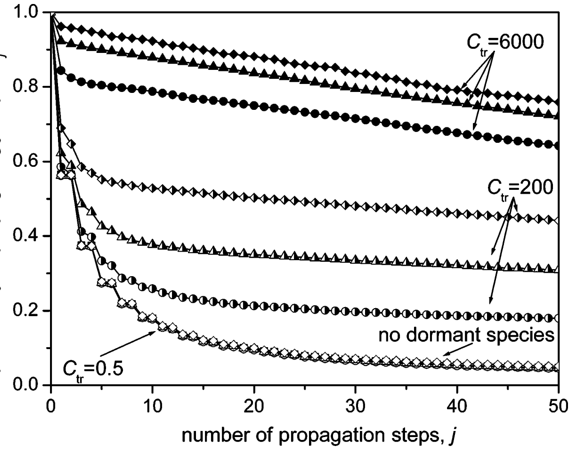


Figure 4. Probability of radicals surviving at least j propagation steps without termination in a system that is zero-one in the absence of an RTA, showing that increasing dormant species concentration has little effect on the behavior of the system at low RTA activity (when transfer is quite unlikely regardless of the concentration of RTA) and at high RTA activity (when transfer is quite likely). The behavior of three different RTAs is shown here at three different concentrations in the particles: [D] = 3 mM (circles), 8.5 mM (triangles), 20 mM (diamonds). For all curves, $r_s = 50$ nm and $X_d = 100$.

implies, inter alia, that with long dormant chains the amount of polymer produced per radical is increased by the presence of the RTA and that the living nature of the system is enhanced by the CLD termination reaction.

At higher conversions (i.e., longer dormant chains), it would appear that particles of all sizes are able to support more radicals than they would have been able to in the absence of the RTA. While this increase may be only small (depending on the particle size), it will inevitably lead to an increase in $\bar{n}$, hence also the rate of polymerization. The physical reasons for this result and the implications for interpreting experimental data are discussed below.

Influence of Dormant Chain Concentration. As illustrated in Figure 4, the addition of the high-activity RTA gives approximately the same result, regardless of the concentration of the RTA. On the other hand, the low-activity RTA tends to have little effect on the lifetime of the radicals at all, the P_j versus j curves being unaffected by its presence over a range of [D].

This is readily understandable when the likelihood of the transfer reaction occurring is estimated as follows. Consider the expression for the probability of the transfer to *any* dormant reaction occurring:

$$P(\mathrm{P}^{\bullet} + \mathrm{D}) \approx \frac{k_{\mathrm{tr,D}}[\mathrm{D}]}{k_{\mathrm{p}}C_{\mathrm{p}} + \langle k_t \rangle / N_{\mathrm{A}}V_{\mathrm{s}} + k_{\mathrm{tr,D}}[\mathrm{D}]} \qquad (11)$$

For a given working range of [D], this expression has two obvious limits: when $k_{\mathrm{tr,D}}$ is so large as to give $P(\mathrm{P}^{\bullet} + \mathrm{D}) \approx 1$ and when $k_{\mathrm{tr,D}}$ is so small as to give $P(\mathrm{P}^{\bullet} + \mathrm{D}) \approx 0$. For values of $k_{\mathrm{tr,D}}$ large (or small) enough to approach these limits, the actual value of [D] becomes irrelevant. In Figure 4, the activity of the RTAs span 4 orders of magnitude, exploring both these limits; hence, a factor of 3 variation in [D] while large in practical terms, is small by comparison. Only for the midrange activity RTA is $P(P + D)$ not in one limit or the other; there is only a small window of values for C_{tr} for which [D] will have a direct effect on the reaction.

Moving from the mathematical description to the physical processes involved, the high-activity RTA tends to always result in transfer to the dormant species as the probability of transfer occurring (from eq 11) is close to unity, regardless of the concentration of the RTA (over the working range under consideration). On the other hand, the low-activity RTA has a probability of transfer approaching zero, so it plays no part in the reaction sequence even at high concentrations. In the intermediate-activity RTA, the pseudo-first-order rate coefficients for propagation and transfer to dormant species are of similar order, so the system does not lie in either of the above limits for the probability of transferring. The result is that for the intermediate-activity RTA, [D] plays a more significant role in the reaction sequence at higher concentrations than it does at lower concentrations, as seen in the concentration-dependence for P_j versus j in Figure 4.

There may, however, be an indirect effect of [D] on the reaction, through its influence on the dormant chain length. For a high-activity RTA, X_{d} is related to the conversion by the simple relation:

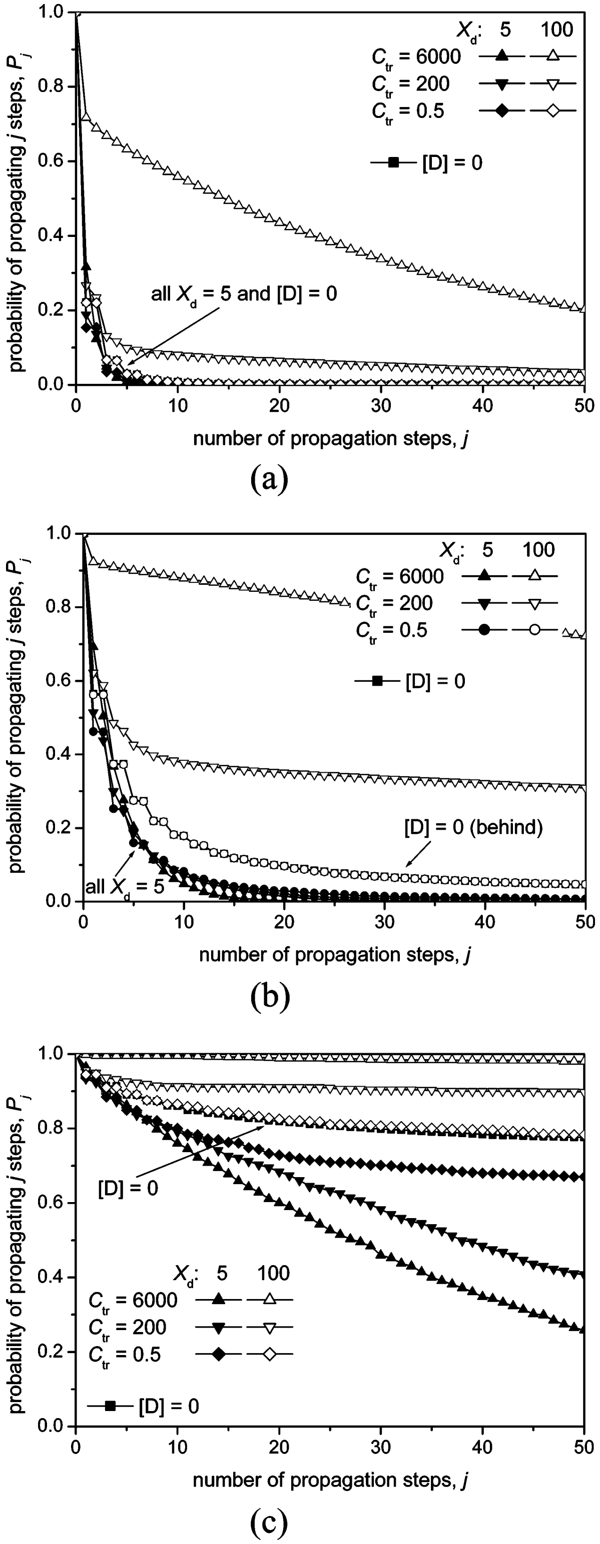
$$X_{\mathrm{d}} = \frac{x[\mathrm{M}]_0}{[\mathrm{D}]} \qquad (12)$$

(neglecting termination and initiator-derived radicals). With increasing [D], short chains take longer (in terms of conversion) to grow (i.e., $\mathrm{d}X_{\mathrm{d}}/\mathrm{d}x = [\mathrm{M}]_0/[\mathrm{D}]$), and the effects of short chains last until higher conversions. For many RTAs, the effect of higher [D] may thus only be seen through the reduction in X_{d} at any given conversion rather than an intrinsic effect of [D] on the reaction kinetics.

Influence of Chain Transfer Constant. The value of C_{tr} has been found experimentally to have a significant effect on the behavior of RTA-mediated emulsion polymerizations, although the nature of this effect is not clear.[11] Figure 5 shows that this effect is quite conversion-dependent, explaining the difficulty that has been experienced in accurately quantifying these effects. Moreover, the nature of the effect reverses from low to high conversion.

At low conversion (e.g., $X_{\mathrm{d}} = 5$ in Figure 5), the higher the activity of the RTA, the shorter the lifespan of the two radicals in the particle. At higher conversion (e.g., $X_{\mathrm{d}} = 100$), the higher the activity of the RTA, the longer the lifespan of the two radicals. In particular, for particles of the $r_{\mathrm{s}} \approx 50$ nm size, zero-one kinetics would still appear to be a valid description of the system for only the low-activity RTAs, with higher activity RTAs causing significant deviation from the pseudo-instantaneous termination requirement leading to a loss of "zero-one-ness". This effect will be discussed at some length below.

In considering Figure 5, it must be noted that a physical system for $X_{\mathrm{d}} = 5$ with a low-activity RTA is unlikely to be achievable, as the probability of transfer to dormant species is quite low, so the dormant chains tend always to be significantly longer. This situation may, however, be a reasonable approximation to the system in which there is a (roughly) bimodal distribution of dormant species of the initial unreacted RTA and dormant species of length $\bar{M}_{\mathrm{n}}$. The modeling work of Adamy et al.[47] illustrates how a low-activity RTA is consumed over the course of the entire reaction, not in the first few percent conversion as in a high-activity



(a)

(b)

(c)

Figure 5. Probability of radicals surviving at least *j* propagation steps without termination, showing the influence of the RTA activity at various different particle sizes. Note that for the low-activity RTA, $X_d = 5$ is an unphysical situation, but it may give some indication of the behavior of the initial RTA before the polymeric adduct is formed. (a) $r_s = 30$ nm, (b) $r_s = 50$ nm, (c) $r_s = 120$ nm. Note that a and b follow zero-one kinetics in the absence of an RTA. For all simulations, [D] = 8.5 mM.

RTA.[17] Of course, the leaving group from the initial RAFT agent, R$^\bullet$, is of a different nature to the leaving group from later adducts, $P_i^\bullet$. The effects of this are quite profound as discussed recently by Chong et al.[59]

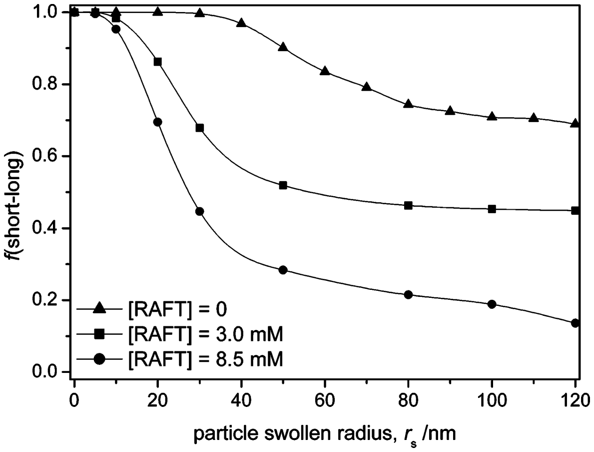


Figure 6. The fraction of all termination reactions that were short–long reactions shown as a function of r_s. The presence of RTA leads to a significant decrease in the proportion of termination that occurs through a short–long reaction; however, the amount of short–long termination is vastly greater than the population of short dormant chains. Other simulation parameters: $X_d = 100$, $C_{tr} = 6000$.

Chain Length of Terminating Species. The chain lengths of the two polymeric radicals involved in the termination reaction give an important insight into the kinetics of particle growth. The proportion of termination reactions that are short–long varies as a function of particle size, as shown in Figure 6. For the purposes of this study, short–long reactions are taken to be those involving a chain 10 units in length or less and a chain of length 100 units or more.

In the case of an $r_s = 50$ nm particle with a high-activity RTA at [D] = 8.5 mM, Figure 6 indicates that 28% of termination reactions are short–long, even though the short chain is only 0.037% of the chain population (radical activity being transferred around all chains through eq 3). Noting from Figure 3b that significant amounts of polymer are made in the presence of two radicals in such a system, it may be deduced that the short terminating species must be reactivated short chains, not directly entered species. Transfer of radical activity back to the short (e.g., *z*-meric) RTA adduct is thus a common precursor to termination. That the entering species is always a short, *z*-meric radical (and not a radical with length dependent on conversion) is thus quite an important facet of the system.

Figure 6 gives no direct indication of the actual amount of termination (or the radical lifetime) in each system, simply the proportion of termination reactions that were short–long reactions. As the proportion of long–long termination reactions increases, however, the lifetime of the radicals in the particle would be expected to increase, as long–long termination is a slower process.

Discussion

The CLD effects outlined above indicate that the kinetics of RTA-mediated living radical polymerization are far more complicated than those of classical polymerizations. This is exemplified here by the study of emulsion polymerizations, where the factors controlling the kinetics of particle growth are changed by the presence of an RTA. In a system without RTA, the primary factor controlling whether a given particle will follow zero-one kinetics is the particle size r_s, with conversion having a secondary effect through its influ-

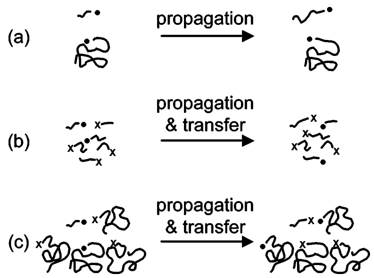


Figure 7. Schematics illustrating the influence of the RTA moiety (marked ×) on the CLD termination reactions between polymeric radical species (marked $^\bullet$) in three limiting cases (a) no RTA, (b) early in the reaction (all dormant chains short), and (c) late in the reaction (dormant chains are long).

ence on w_p (w_p tends to remain constant during Intervals I and II of the emulsion polymerization when monomer droplets are still present[12]). In the presence of RTA, however, the conversion may play a significant part in determining the appropriateness of zero-one kinetics, since for high-activity RTAs, the lengths of the dormant chains are conversion dependent. The secondary influence of conversion on w_p is also present (as all the diffusion-controlled reactions slow with increasing w_p) and the concentration of dormant species and the activity of the RTA must also be taken into account when evaluating the applicability of zero-one kinetics.

Most of the well-studied classical emulsion polymerization systems may be neatly classified as following either zero-one or pseudo-bulk kinetics, with comparatively few systems lying in the area between these two limits. Moreover, gross physical changes such as the addition of an inert diluent or polymerization to high conversion are required to change a system from one limit to the other.[12] In the high-activity RTAs, a very small amount of the RTA (e.g., 2 mM) is sufficient to cause a system to start as zero-one then change in kinetics to something that is neither zero-one nor pseudo-bulk (and remain in that difficult-to-describe state for a large portion of the reaction time), finally becoming pseudo-bulk (with possibly a reduced value of the pseudo-first-order rate coefficient for termination) at high conversion. The profound impact of the RTA on the kinetics of particle growth may only be explained with a closer analysis of the chain-length dependent processes involved.

Origin of CLD Effects. The influence of RTAs on polymerization systems is readily explained by considering the chain lengths of the various reacting species and the chain-length dependence of the reaction rates. Several situations may be constructed that illustrate the limits of the behavior shown above. These limits, illustrated in Figure 7, will be introduced and discussed in turn.

No RTA Present. In the case where $[D] = 0$, the radical activity always remains on a short chain, the length of the polymeric radical chain changing only by propagation. All termination reactions are thus between the short, recently entered radical and the long, preexisting radical, with termination rate coefficient $k_t^{\text{short}-\text{long}}$, and are relatively fast. This situation is shown in Figure 7a and forms the basis for the analytic model of Maeder and Gilbert.[34] The stepwise probability of an *i*-meric radical propagating (hence not terminating) increases with each step; as the short chain grows longer it is less likely to terminate because its diffusion rate decreases so it is less likely to collide with other chain ends. In terms of eq 1 and 4, $P(P_{i+1}^\bullet + M) > P(P_i^\bullet + M)$ (see the Appendix for further details).

High-Activity RTA with Short Dormant Chains (i.e., Low Conversion). The case where C_{tr} is large and X_d is small presents itself in Figure 7b. In this case, both the entering and preexisting radicals are short (the preexisting radical and the dormant chains are the same length, owing to the RTA equilibration reaction, eq 3). Termination in this system is a short−short reaction ($k_t^{\text{short}-\text{short}}$), hence faster than would be expected in the absence of RTA.

Moreover, the chain length of the polymeric radical does not increase at a rate of k_pC_p, as the transfer to dormant species reaction will tend to keep the chain lengths of the radicals relatively constant in the short term. More formally, the radical length increases at a rate of approximately $k_pC_p/([D]N_AV_s)$, where $[D]N_AV_s$ is the number of RTA moieties in the particle. Given that $[D]N_AV_s$ is typically 10^2-10^5 in these systems, the length of the propagating radical changes more slowly by a similar factor. The result of this is that the stepwise probability of an *i*-meric radical propagating and not terminating does not increase as it does in the absence of RTA, $P(P_{i+1}^\bullet + M) \approx P(P_i^\bullet + M)$, (indeed, for all values of r_s and [D] studied here, it remains essentially unchanged over the entire simulation). As a consequence, the lifetime of the radical is reduced further. Any process that leads to a buildup of short dormant chains (no matter what length the other dormant chains are) would be expected to decrease radical lifetime significantly.

High-Activity RTA with Long Dormant Chains. In contrast to the previous limit using short chains, in the case where C_{tr} is large and X_d is also large, radical lifetimes are increased by the addition of the RTA. As illustrated in Figure 7c, the entering radical transfers rapidly to one of the longer dormant chains, creating a short dormant chain. This means that termination requires either a long−long reaction, $k_t^{\text{long}-\text{long}}$, or transfer of radical activity back to the short dormant chain. Both long−long termination and transfer back to one specific dormant chain are less likely to occur than propagation, so the termination reaction is suppressed.

Figure 6 shows that transfer of radical activity back to the short dormant chain is a significant route to termination, accounting for far more termination reactions than would be expected from population balance alone (reinforcing the inference from diffusion-controlled kinetics that long−long termination is slow). Compartmentalization of the radicals into different particles and chain-length dependent reactions cause an increase in the lifetime of the radicals in the particles and, inter alia, an increase in the amount of polymer produced per radical. As concluded from studies of other living free-radical polymerization systems,[60] the living nature of the system may be enhanced by the CLD transfer and termination reactions. However, this effect is only seen for high-activity RTAs and with long dormant chains.

Low-Activity RTA. The final limit to be discussed here is when C_{tr} is small. That transfer to dormant species happens infrequently also means that the RTA induces few CLD effects on the kinetics of polymerization (e.g., on particle growth), as the length of the polymeric radicals involved in the termination reactions is, for the most part, unaffected by the presence of RTA.

Experimental Comparison

At this point, it is instructive to consider the qualitative understanding achieved here in terms of the conversion versus time data obtained by Prescott et al.[18] for a high-activity RAFT agent (2-phenylprop-2-yl phenyldithioacetate, PPPDTA) in the emulsion polymerization of styrene with $r_s = 52$ nm and $[D] = 16$ mM. In the original paper, data for $\bar{n}$ were not reported; however, it is relatively simple to infer some characteristics from the reported data as follows. It was noted by Prescott et al.[18] that the rate of polymerization was reduced through the addition of the RAFT agent. Since $\bar{n} \propto R_p$ (and C_p at the beginning of the reaction is the same), it may be readily concluded that $\bar{n}$ is reduced by the addition of the RAFT agent. Moreover, an approximately constant rate of polymerization was observed (Figure 5 in ref 18), even though the concentration of monomer was decreasing with conversion. Since $R_p \propto C_p\bar{n}$, constant R_p and decreasing C_p indicates $\bar{n}$ increases with conversion.

On this basis, the data of Prescott et al.[18] have three key characteristics:

(1) At low conversion, $\bar{n}$ is less than that of the non-RAFT system.

(2) In the presence of RAFT, an increase in $\bar{n}$ is evident throughout the experiment (noting that the experiments described were Interval III experiments so the concentration of monomer is decreasing throughout).

(3) An inhibition period is observed that decreases with increasing initiator concentration but is not observed in the equivalent bulk system.[61,62]

The CLD kinetics presented here offer for the first time some explanation of observations 1 and 2. Importantly, the CLD approach used here has established that these particles are not zero-one at intermediate to high conversions, so that mechanisms such as termination of intermediate radicals may for the first time be validly considered in these systems (as particles such as these were previously presumed to follow zero-one kinetics by analogy to the identical non-RAFT systems,[17,18] there was no ability for reactions involving two radicals within the one particle to affect the particle growth kinetics). A brief qualitative explanation of the observed effects is as follows:

(1) At low conversions, termination is entirely short−short; hence, the lifetime of radicals in two-radical particles is reduced. This leads, inter alia, to a reduction in $\bar{n}$.

(2) As conversion increases, the length of the dormant chains increases, leading to an increase in the ability for particles to support more than one radical and giving, inter alia, an increase in $\bar{n}$.

The recent work of Ferguson et al.[19] provides working RAFT/emulsion systems that display few, if any, of the previously published deficiencies. The RTA used by Ferguson et al.[19] is of the form of an amphipathic polymer/RAFT agent adduct of the form $(AA)_x-(BA)_y-S-C(Z){=}S$. The adduct form of the RTA is thus already of significant length (at least 5−10 units) before becoming part of the latex particle. By having longer dormant chains in the initial stages of polymerization, the lifetime of the radicals is not reduced to the same extent as a system using a short-chain RAFT agent; indeed, Figure 3 suggests that once X_d reaches 5−10 units, small particles begin to lose their zero-one character. At low conversions, the system used by Ferguson et al.[19] has both small particle sizes (from the micelles of amphipathic RAFT agent) and short dormant chains; however, in small particles, the effects of the RTA are also the least pronounced (Figure 3a and 5a). The combination of polymeric RTA adducts and small particles (along with a well-chosen RAFT/monomer pair) thus mitigates the potentially harmful effects of CLD kinetics within the system.

RAFT-mediated miniemulsion polymerizations of styrene and methyl methacrylate have also shown improved rates of polymerization through the use of oligomeric RAFT adducts.[3] The work of Lansalot et al.[63] showed that the rate of polymerization was increased (approaching that of the non-RAFT system) by the use of a polystyrene-RAFT adduct with molecular weight of around 2000; similarly, the work of Butté et al.[64] showed similar results with polystyrene-RAFT and poly(methyl methacrylate)-RAFT adducts. However, drawing conclusions from these data is not easy. Possible interpretations include (a) the importance of CLD termination, as described here; (b) the importance of exiting radicals (the longer R group from the adduct is unable to exit the newly nucleated droplet);[63] (c) the "hyperswelling" of nucleated droplets by very short, oligomeric chains from a conventional RAFT agents.[65] Clearly, since the particle size distribution is changed by the oligomeric-RAFT adducts (thus changing the rate of polymerization, since in a compartmentalized system, the rate of polymerization is proportional to the number of particles in the system), it is easy to overinterpret these data to show support for almost any mechanism. It suffices to note that these data are consistent with the thesis put forward here that CLD termination plays an important role in RTA-mediated polymerizations.

Importantly, the work reported here affirms that the use of zero-one kinetics was appropriate in the recent kinetic investigation of low-activity xanthate-based RAFT agents performed by Smulders et al.[15] The kinetic investigations reported by Smulders et al.[15] made use of zero-one kinetics to obtain the rate coefficients for radical entry and exit in latex particles containing xanthates. By way of comparison, this work also indicates that zero-one kinetics would be inappropriate for the high-activity RAFT agents of Prescott et al.,[18] except at low conversions.

Implications for Experimental Design. The ultimate goal of this work is to find conditions to improve the performance of RTA-mediated polymerizations such as the RAFT polymerizations performed by Monteiro et al.[17] and Prescott et al.[18] While the field of RAFT/emulsion polymerization has progressed significantly since the pioneering work of Monteiro et al.,[17] there remain significant unexplained difficulties.[11]

The arguments presented here, along with the experimental work discussed above, provide a basis on which RAFT (and other RTA) experiments may be designed. Indeed, the following points may be beneficial to this process:

Long-chain dormant species lead to an increased lifetime for the radicals compared to short-chain dormant species. Use of an oligomeric RTA-adduct is thus an advantage.

[D] has little direct effect on the lifetime of the propagating radicals; as illustrated in Figure 4, the high-activity RTA tends to always result in transfer to the dormant species, regardless of the concentration of the RTA, while the low-activity RTA tends to play no part in preventing the termination reaction from occurring. There is only a small range of values for C_{tr} for which [D] will have an effect.

[D] may have a secondary effect on the kinetics of polymerization with high-activity RTAs. An increased [D] will mean that it takes longer to progress from short dormant chains to longer dormant chains as shown in eq 12. This results in the retarding effects of short chains lasting for longer into the polymerization; hence, there may be a retardation that is dependent on [D].

As previously reported, the low-activity RTAs may be incorporated into the polymerization with little effect as they would appear not to influence the kinetics of polymerization (notwithstanding the surface-activity arguments of Smulders et al.[15] that indicate a profound effect on emulsion polymerization using xanthates).

In an emulsion polymerization, zero-one kinetics may be appropriate for the initial stages of the experiment but are unlikely to be applicable thereafter; pseudo-bulk kinetics may be appropriate (but with a reduced pseudo-first-order termination rate coefficient) at later stages in the experiment. However, there are cases when neither zero-one nor pseudo-bulk kinetics are applicable.

For kinetic studies, it is important to realize that RTA-mediated polymerizations have rate coefficients (e.g. ($\langle k_t \rangle$) that change by orders of magnitude over the course of the reaction.

Conclusions

The Monte Carlo model presented here provides significant insights into the relative importance of the different processes (propagation, transfer to dormant species, and termination) and an indication of the influence of CLD kinetics in both heterogeneous and homogeneous polymerization systems. From this work, it is evident that in all modeling of RTA-mediated systems, CLD kinetics *must* be considered. Moreover, the effect of the RTA changes as a function of the chain length of the dormant species. For a high-activity RTA, the kinetic behavior of the system changes markedly (indeed, it reverses) as a function of conversion, reducing the lifetime of the radical at low conversion when short-chain lengths dominate the system, while increasing radical lifetime at higher conversion when longer dormant chains are present.

The specific effects that were reported here may be explained in terms of CLD termination reactions and the way in which the RTA changes the chain length. In summary, high transfer constant RTAs and short dormant chains exhibit significantly shorter radical lifetimes because of the increased termination rate coefficient, $k_t^{\text{short-short}}$. Long dormant chains, however, may lead to an extension of radical lifetimes, because of the reduced termination rate coefficient, $k_t^{\text{long-long}}$.

In designing RTA-mediated polymerizations, long-chain dormant species provide a considerable advantage, as they lead to an increased lifetime for the radicals compared to short-chain dormant species. The oligomeric RTA-adducts of Ferguson et al.[19] provide an example of suitable long-chain RTAs. While this work has identified changes to the nature of the termination reaction in RTA systems (both emulsion and bulk/solution polymerizations) on the basis of chain-length dependent kinetics, other mechanisms that alter radical entry or exit in emulsion polymerizations may also lead to changes in the system behavior.

There are also significant implications from this work for the kinetic study of RTA systems such as RAFT-mediated polymerizations. The continually changing CLD rate coefficients for termination, in particular, make the use of average values for parameters such as k_t fraught with difficulties. Additionally, zero-one kinetics are often inapplicable to RTA/emulsion systems, as are pseudo-bulk kinetics, with the nature of the kinetic scheme changing throughout the reaction. This suggests that the investigation of zero-one-two kinetics[66] in RTA/emulsion systems may be a worthy pursuit, as is investigating the influence of distributions of chain lengths for the dormant species.

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Appendix

Analytic Understanding of CLD Termination in Emulsion Polymerization. Following the earlier work of Maeder and Gilbert,[34] consider a latex particle containing one preexisting radical. Upon entering a particle, a second radical species may undergo several different reactions, including propagation, termination, and transfer to monomer. Of principal interest in determining the appropriateness (or otherwise) of zero-one kinetics to a system are the propagation and termination reactions.[34] Since termination has been shown to have significant chain-length dependence (especially above the concentration of polymer where chains are entangled, c^{**}),[67] the probability that a chain will continue to survive in a particle containing another radical increases as propagation continues, $P(P_{i+1}^{\bullet} + M) > P(P_i^{\bullet} + M)$.

The reactions that are included in this test of zero-one kinetics (including their chain-length dependent rate coefficients) are shown in eqs 1 and 2, above. For a particle containing two radicals (one recently entered and the other preexisting), there will be a considerable difference in the lengths of the radical chains. The recently entered radical will be short (hereafter, the *i*-mer), while the preexisting radical will be quite long and may be denoted as an L-mer. In a particle of swollen volume V_s, containing one radical $P_i^{\bullet}$, $[P_i^{\bullet}] = 1/(N_A V_s)$ where N_A is Avogadro's constant. The pseudo-first-order propagation rate for an *i*-mer is given by $k_p{}^iC_p$ (where C_p is the concentration of monomer in the particle) and the pseudo-first-order termination rate is given by $k_t{}^{iL}/N_AV_s$. This expression (and eq 17) for the termination rate follows the IUPAC convention of $d[P_i^{\bullet}]/dt = -k_t{}^{ij}[P_i^{\bullet}][P_j^{\bullet}]$ since $i \neq j$; *i* is by definition small whereas *j* represents the "long", preexisting chain.

The probability that an $(i-1)$-*mer will propagate to an* i-mer, $P_{i-1\to i}$, (a probability conditional on the presence of a $P_{i-1}^{\bullet}$) is thus given by

$$P_{i-1\to i} = \frac{k_p^{\,i-1}C_p}{k_p^{\,i-1}C_p + k_t^{\,i-1,L}/N_AV_s} \tag{13}$$

As noted in the body of the paper, the length of the newly entered radical may be found using the Maxwell–Morrison model for entry.[51,52] In this model, the entering species is a z-meric radical where z is the critical degree of polymerization for the oligoradical to become surface active. For hydrophobic monomers with a charged initiator end-group, z is quite small, for example, styrene with a persulfate initiator has $z = 2$ or 3.[52,53]

Following the notation of Maeder and Gilbert,[34] the probability of an entering z-mer propagating to at least a j-mer without undergoing termination is written as P_j. The probability of an entering z-mer propagating to a z+1-mer is $P_{z\to z+1}$ (i.e., $P_{(z+1)-1\to(z+1)}$); hence, P_j is the product from $P_{(z+1)-1\to(z+1)}$ to $P_{j-1\to j}$:

$$P_j = \prod_{i=z+1}^{j}\left(\frac{k_p^{\,i-1}C_p}{k_p^{\,i-1}C_p + k_t^{\,i-1,L}/N_AV_s}\right) \tag{14}$$

which may be rearranged to give

$$P_j = \prod_{i=z}^{j-1}\left(\frac{k_p^{\,i}C_p}{k_p^{\,i}C_p + k_t^{\,iL}/N_AV_s}\right) \tag{15}$$

This expression is subtly different to that previously published by Maeder and Gilbert.[34] In the original formulation of this work, Maeder and Gilbert wrote P_j with an upper limit for the product of j instead of $j-1$ as derived for eq 15:

$$P_j^{\,\mathrm{wrong}} = \prod_{i=z}^{j}\left(\frac{k_p^{\,i}C_p}{k_p^{\,i}C_p + k_t^{\,iL}/N_AV_s}\right) \tag{16}$$

The above expression P_j^{wrong} fails two consistency tests:

(1) Equation 16 implies that the probability of generating a radical that is j units long depends on $k_p^{\,j}$; however, the behavior of the j-mer is irrelevant to whether the j-mer is ever formed.

(2) When P_z is calculated from eq 16, the value obtained is not unity. The probability of having a z-mer in the particle when a z-mer has entered the particle should be unity.

In essence, eq 16 includes the generation of a j+1-mer from a j-mer (hence the dependence on $k_p^{\,j}$). The result is that the curves published elsewhere for the probability of propagation to a j-mer are consistently shifted to the left of those given by eq 15.

Estimating the value of the termination rate coefficient can be quite difficult; both experimental results[68] and theoretical arguments[26] indicate that diffusion control appears to be a reasonable approximation in emulsion polymerization systems. A Smoluchowski expression for the diffusion-limited reaction may thus be written in terms of the diffusion coefficient, D^{iL}. The expression obtained for $k_t^{\,iL}$ is (where once again $i \neq L$):

$$k_t^{\,iL} = 4\pi D^{iL} p^{iL} \sigma N_A \tag{17}$$

where p^{iL} is the probability that the two radicals will undergo termination when within a capture distance σ. The parameter p^{iL} accounts for the need for the two radicals to have opposite spin to undergo termination and is usually taken to be $^1/_4$. With the IUPAC recommended kinetic scheme for termination shown in eq 2, $k_t^{\,iL}$ has a factor of 4 in the expression not a factor of 2 as in the slightly different formulation of Russell et al.[40] The original calculations of Maeder and Gilbert[34] incorrectly used the expression of Russell et al.[40]

The mutual diffusion coefficient may be constructed from the center-of-mass diffusion coefficients for each species, $D_i^{\,\mathrm{com}}$ and $D_L^{\,\mathrm{com}}$, and the reaction–diffusion coefficient for each chain, $D_i^{\,\mathrm{rd}}$ and $D_L^{\,\mathrm{rd}}$:[49]

$$D^{iL} = D_i^{\,\mathrm{com}} + D_L^{\,\mathrm{com}} + D_i^{\,\mathrm{rd}} + D_L^{\,\mathrm{rd}} \tag{18}$$

The center-of-mass diffusion coefficient for the long polymeric chain is so slow above c^{**} as to be negligible compared to that of the shorter chain. To quite a good approximation, the reaction–diffusion term will be independent of chain-length,[49] giving

$$D^{iL} = D_i^{\,\mathrm{com}} + 2D^{\mathrm{rd}} \tag{19}$$

where D^{rd} is given by

$$D^{\mathrm{rd}} = k_pC_pa^2/6 \tag{20}$$

Here, a is the root-mean-square end-to-end distance per square root of the number of monomer units in the polymer chain. Suitable values for a (and σ) for various monomers are given by Russell et al.[49] In practice, D^{rd} is often much smaller than $D_i^{\,\mathrm{com}}$, so this term may be neglected in the calculation when i is sufficiently small.

The work of Griffiths et al.[43] provides a suitable method for calculating $D_i^{\,\mathrm{com}}$. Although the empirical scaling law developed by Griffiths et al.[43] does not necessarily provide significant physical insight, it does permit the calculation of the $D_i^{\,\mathrm{com}}$ as a function of the weight fraction of polymer, w_p.

The scaling laws developed by Griffiths et al.[43] take two parts. For the case of the diffusion of the monomer in the polymer matrix, $D_1^{\,\mathrm{com}}$, the relationship with fitting parameters c_i:

$$D_1^{\,\mathrm{com}}/(\mathrm{cm}^2\ \mathrm{s}^{-1}) = c_0 - c_1w_p + c_2w_p^{\,2} + c_3w_p^{\,3} \tag{21}$$

gave good results over a wide variety of values for w_p for various monomers including styrene,[33] and butyl methacrylate.[43] Furthermore, the CLD of $D_i^{\,\mathrm{com}}$ was found by Griffiths et al.[43] to fit the expression

$$\frac{D_i^{\,\mathrm{com}}}{D_1^{\,\mathrm{com}}} = i^{-(0.664+2.02wp)} \tag{22}$$

over a variety of monomers and values for w_p. The rate coefficient for termination is thus readily obtained from eq 17.

Chain Transfer Coefficient of *n*-Butyl Acrylate. The model development of Maeder and Gilbert[34] has provided a useful tool for the evaluation of whether a system follows zero-one kinetics. In this method's original application to an *n*-butyl acrylate system, the conclusions as to the applicability of zero-one kinetics were erroneous. Using the revised model (presented above) and corrected input parameters, it is found that

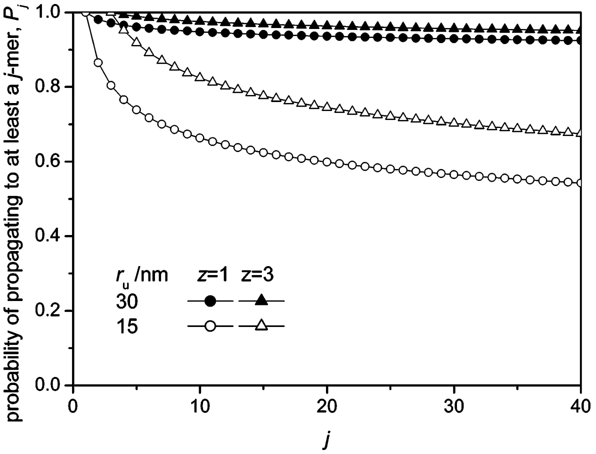

Figure 8. The probability of propagation to a *j*-mer in 15 and 30 nm unswollen radius particles for both entering monomeric and trimeric radicals. Curves generated using the analytic technique (eq 15) using the parameter values of Maeder and Gilbert[34] with the IUPAC expression for k_t^{iL} (eq 17) and the value of σ from Russell et al.[49]

the system was not zero-one. However, the value for the chain transfer coefficient for *n*-butyl acrylate is believed to be no less accurate.

The probability of propagating to a given chain length in the *n*-butyl acrylate test particles used by Maeder and Gilbert[34] is shown in Figure 8. Here, the same parameters are used as in the original work by Maeder and Gilbert,[34] with the exception of the value of $\sigma = 7$ Å from Russell et al.[49] The IUPAC expression for k_t^{iL} (eq 17) was used in conjunction with the analytic technique (eq 15).

It is evident from Figure 8 that zero-one kinetics are not appropriate for the *n*-butyl acrylate emulsion polymerizations of unswollen radius, $r_u = 15$ nm, as a significant amount of polymer may be formed in a two-radical environment. In their original paper, Maeder and Gilbert[34] noted that with the known values of k_p, k_{tr}, and a pseudo-first-order rate coefficient for radical entry, ρ, they were unable to calculate the observed value for $\bar{n}$ to a factor of 25. Moreover, their observed value of $\bar{n}$ lay between that predicted by zero-one kinetics and that predicted by pseudo-bulk kinetics. It has been noted elsewhere that for low-$\bar{n}$ systems, the value of $\bar{n}$ obtained from the pseudo-bulk equation is an underestimate of the true $\bar{n}$ of the system, owing to the effects of compartmentalization on the system and the inappropriateness of the simplification $\overline{n^2} - \bar{n} = \bar{n}^2$ when $\bar{n}$ is small.[69] The use of a zero-one-two model[66] would provide a value for $\bar{n}$ closer to the experimentally determined value.

The importance of whether the particles were zero-one to the original work of Maeder and Gilbert[34] must also be considered. The analytic model used here was developed by Maeder and Gilbert so as to establish that their system was zero-one; hence, transfer to monomer was the primary chain-stopping event, not the termination of two radicals (thus permitting k_{tr} to be calculated from a linear section of the molecular weight distribution). It will now be shown that this condition is still met, even though the system in question is not zero-one.

To estimate the proportion of particles that contain two radicals (and hence the amount of polymer produced in a two-radical environment), it is instructive to consider other kinetic schemes for particle growth. While pseudo-bulk kinetics is not necessarily applicable to the situation at hand (see Figure 8 and the calculations by Maeder and Gilbert for $\bar{n}$ of their system with pseudo-bulk kinetics), it does provide a useful comparison. In the low-$\bar{n}$ limit of pseudo-bulk kinetics, it may be shown (using the steady-state assumption for the N_0 species and subsequently calculating $\bar{n}$ from the N_i) that the ratio N_0:N_1:N_2 (where N_i is the population of particles containing *i* radicals) is approximately 1:$\bar{n}$:$\bar{n}^2$, which evaluates in this case to approximately 1:10^{-3}:10^{-6}. The amount of polymer produced in a two-radical environment is, therefore, small. Moreover, Hawkett et al.[32] established that any system following Smith–Ewart kinetics which has $\bar{n} < 0.1$ in its steady state is exit-dominated and that it is reasonable to neglect bimolecular termination.

On this basis, it is possible to conclude that the vast majority of the chains produced in the *n*-butyl acrylate polymerizations of Maeder and Gilbert[34] do indeed have transfer to monomer as the chain-stopping event; hence, the reported value for k_{tr} is no less accurate for the omissions made in the original paper.

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