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Radical Loss in RAFT-Mediated Emulsion Polymerizations

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ABSTRACT: Radical loss processes in RAFT-controlled emulsion polymerization are investigated using γ-initiated seeded emulsion polymerization of styrene in “relaxation mode”, i.e., following the rate of polymerization after removal from the radical source. This provides direct measurement of radical loss processes. A water-insoluble RAFT agent, 2-phenylprop-2-yl phenyldithioacetate, was transported to preformed seed particles using acetone, the acetone then removed, the particles swollen with monomer, and RAFT-mediated polymerization initiated by γ-irradiation. The systems show good control over the molecular weight of the products and a retardation dependent on the concentration of RAFT agent. Kinetic parameters are obtained from the γ-relaxation experiments, using pseudo-bulk kinetics as an approximation to full compartmentalization/chain-length-dependent kinetics to describe the systems. The rate of radical loss was strongly affected by the presence of RAFT agent and was found to decrease with increasing length of the dormant chain. The interpretation of this observation is as follows. The termination rate coefficient depends on chain length; the dominant mode of termination is the reaction between chains of similar length in RAFT-mediated systems but between short and long chains in conventional systems. Radical entry into particles is assumed to be by chains of degree of polymerization z formed in the aqueous phase. Dormant z-meric chains in the particles are postulated to lead to an increase in the rate of radical exit from the particles, with the reactivation of these species generating a z-meric radical that is able to desorb from the particle surface in a RAFT-induced exit mechanism, leading to the rapid exchange of radicals between particles and hence radical loss. A simple model for the radical loss rate coefficient, expected to be valid for longer chain lengths, both reproduces much more computationally expensive Monte Carlo calculations and (when used with the scaling suggested by reptation theory) gives quantitative accord with the relaxation data.

Introduction

The development of techniques for living free-radical polymerization has provided control over molecular architecture for a variety of monomers, allowing the easy synthesis of block copolymers and polymers with well-defined molecular weight distributions as well as more exotic architectures, such as combs and stars.[1−4] The techniques include nitroxide-mediated polymerization,[5] atom-transfer radical polymerization,[6,7] alkyl halide-mediated polymerization[8,9] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[2,10]

Living polymerization techniques have been successfully applied to many solution and bulk polymerization systems; however, application of living polymerization to emulsion polymerization has encountered numerous difficulties. Emulsion polymerization should, in principle, make it possible to obtain higher molecular weights and faster rates of polymerization compared to homogeneous systems as well as presenting other technical and environmental benefits (such as minimal changes in viscosity for high polymer loadings).[11,12] The main difficulties have been in maintaining colloidal stability, achieving reasonable reaction rates and controlling molecular weight polydispersity.

Significant advances have been made with the seeded emulsion polymerization by Prescott et al.[13] and the ab initio polymerizations of Ferguson et al.[14,15] as the first implementations of RAFT in emulsion polymerization to avoid the above-mentioned difficulties. These systems were developed by explicitly designing systems in which (a) transport of the RAFT agent through the continuous phase is not required during polymerization and (b) polymerization in droplets is avoided.

A reduction in the rate of polymerization is seen in many RAFT-mediated reactions, possibly due to the slow fragmentation of the intermediate bipolymeric radical,[16−18] irreversible and reversible[3,19] termination of the intermediate radical, and the influence of chain-length-dependent (CLD) termination.[20] Interestingly, there is a factor of ~10^6 difference in the expected concentration of the intermediate radical species between these models, a point that has widened the debate rather than resolved it.[21−23]

The essential steps in RAFT polymerization are

$$\mathrm{P}_m^{\bullet} + \mathrm{Z{-}C({=}S)S{-}P}_n \rightleftharpoons \mathrm{Z{-}C^{\bullet}({-}SP}_n\mathrm{)S{-}P}_m \rightleftharpoons \mathrm{Z{-}C({=}S)S{-}P}_m + \mathrm{P}_n^{\bullet}$$

Retardation due to reactions of the intermediate bipolymeric radical $\mathrm{Z{-}C^{\bullet}({-}SP}_n\mathrm{)S{-}P}_m$ is dependent on the nature of the RAFT agent being used, in particular the stability of the intermediate radical through the action of the stabilizing group of the RAFT agent, Z. In the case of a benzyl-activated RAFT agent, such as the one used by Prescott et al.[13] and the trithiocarbonates used

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by Ferguson et al.,[14,15] the intermediate radical is much less stable than that from a phenyl-activated RAFT agent.[18] Retardation due to CLD termination, however, is intrinsic to all living polymerizations.[20]

Monte Carlo modeling suggests that there is significant retardation due to CLD termination in RAFT-mediated polymerizations.[20] The effects of reversible transfer agents, such as RAFT, are expected to be seen in both homogeneous and heterogeneous polymerization systems, the rate coefficients for termination being greater for short chains than for long chains due to their different diffusion rates. The rate of polymerization is reduced by the RAFT agent as it changes the length of the radicals in the polymerization.[20]

The essence of the inferences from this modeling is that RAFT systems differ from conventional free-radical polymerizations because the dominant mode of termination is the reaction between chains of equal length in RAFT-mediated systems but between short and long chains in conventional systems. In summary, at low conversion, the dormant chains are short and the propagating radicals are on short chains, and thus termination is a short−short reaction with high rate coefficient; conversely, at high conversion, the radicals and dormant chains are predominantly long, making termination proceed on the time scale of a long−long reaction with a much reduced rate coefficient.

Conventional (noncontrolled) emulsion polymerization kinetics can be categorized into one of two simple kinetic models: either "zero−one",[12,24] when entry into a particle already containing a growing chain produces instantaneous termination and so intraparticle termination is not rate-determining, or "pseudo-bulk",[12,25] when intraparticle termination is rate-determining and the kinetics are the same as in a bulk, i.e., uncompartmentalized, system. For pseudo-bulk systems, one has

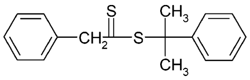
$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \rho_{\mathrm{init}} - 2c\bar{n}^2 \qquad (1)$$

where $c = \langle k_t \rangle / N_A V_s$. Here, $\bar{n}$ is the average number of radicals per particle, ρ_{init} the entry rate coefficient (the frequency at which radicals enter a particle) for radicals derived directly from initiator, N_A the Avogadro constant, and V_s the (monomer-) swollen volume of a latex particle, and $\langle k_t \rangle$ is related to the chain-length distribution of radicals by the usual expression.[26] One also has the Smith−Ewart rate coefficient for exit (the number of radicals lost per particle per unit time by radicals going from the particle to the aqueous phase), k.

In a pseudo-bulk system, $\bar{n}$ can take any value. Common cases are (i) when the value of $\bar{n}$ is so high that each particle effectively behaves as an isolated microreactor and (ii) when the value of $\bar{n}$ is low, exit is very fast and the exited radical rapidly reenters another particle and may grow to a significant degree of polymerization before any termination event. (Pseudo-bulk systems are *not* identical to Smith and Ewart's case 3 kinetics,[27] which are applicable only to systems with $\bar{n}$ significantly above $^1/_2$.)

This convenient zero−one/pseudo-bulk categorization enables rate and molecular weight data to be fitted and interpreted in terms of physical models with a minimum of adjustable parameters (typically no more than two: either ρ_{init} and k or ρ_{init} and c) and has led to considerable mechanistic understanding. However, consideration of CLD termination shows that this useful reduction method cannot readily be used for RAFT/emulsion systems with high-activity RAFT agents.[20] Moreover, it was concluded that the kinetics of polymerization for RAFT/emulsion systems would change throughout the reaction as the length of the propagating radicals changes. The results of Prescott[20] showed that the zero−one model is often inappropriate for RAFT/emulsion systems, in particular in systems with both long dormant chains (i.e. $\bar{M}_n \gtrsim 1000$) and high-activity RAFT agents. While it seems that the zero−one limit is inappropriate for the particular RAFT/emulsion systems studied here and in the Monte Carlo modeling (styrene at 50 °C) except at quite low conversion and with small particles,[20] the applicability of other simplified kinetic schemes remains unclear. In particular, the applicability of pseudo-bulk kinetics is of interest, as this limit provides a simple conceptual understanding of emulsion polymerization and permits kinetic parameters to be determined with a minimum of model-based assumptions.

Scheme 1. Benzyl-Activated RAFT Agent 2-Phenylprop-2-yl Phenyldithioacetate (PPPDTA)



To adequately describe the kinetics of the RAFT/emulsion systems, values of ρ_{init}, c, and k are required, and appropriate account needs to be taken of the fate of exited free radicals. Initiation by γ-radiolysis has particular use for understanding mechanisms in emulsion polymerization, through the study of the changes in polymerization rate after the reactor vessel is removed from the γ-source; this provides direct information about radical loss processes, largely separate from radical creation. These loss processes are termination ones, occurring either entirely within the particles (which is the same process as termination in bulk or solution free-radical polymerization), or termination following exit of a radical from a particle (which is a process peculiar to radical polymerization in dispersed media, such as emulsion polymerization). There is also a minor component from termination with short radicals which are spontaneously generated even in the absence of a radiative or chemical initiator.[28,29]

Here, the results of γ-radiolysis experiments are presented, establishing that RAFT-mediated emulsion polymerization may be successfully undertaken with γ-initiation and are able to provide kinetic data about the RAFT/emulsion systems from relaxation experiments. A semiquantitative treatment of the previously presented Monte Carlo model[20] is also used, with particular emphasis on understanding the γ-radiolysis experiments. The role of compartmentalization of the radicals in RAFT-mediated emulsion polymerization is also investigated, focusing on the possible desorption of oligomeric radicals and the consequences for the kinetic schemes applicable to RAFT/emulsion systems.

RAFT in Seeded Emulsion Polymerization. In a previous study of the kinetics of RAFT/emulsion systems, the seeded emulsion polymerization of styrene with persulfate initiator and mediated by the benzyl-activated RAFT agent PPPDTA (Scheme 1) was followed by dilatometry.[13] The seed particles were synthesized by conventional (non-RAFT) means, and the PPPDTA was transported into the particle by acetone, which was subsequently removed from the system by rotary evaporation; the result is a well-characterized monodisperse latex in which RAFT agent is located entirely inside the particles. In that initial study, it was reported that the rate of polymerization was reduced by the addition of the RAFT agent and that the degree to which the rate of polymerization was reduced was dependent on the ratio of initiator to RAFT agent used. The system showed good control of molecular weight, no formation of colored, oily layers, and no loss of colloidal stability.

RAFT Polymerization with γ-Initiation. Dithioester-mediated polymerizations using γ-initiation have been investigated by Hong et al.,[30] the "iniferter" process being proposed as the mechanism by which polymerization was mediated. Quinn et al.[31,32] subsequently demonstrated that these polymerizations were mediated by the conventional RAFT process, showing the successful RAFT-mediated polymerization of several monomers with various dithioesters in bulk and solution polymerization systems. In addition, there have recently been reports of the successful γ-initiated emulsion polymerization of styrene mediated by xanthates.[33]

The RAFT agent used in this study, PPPDTA, has been used in the successful emulsion polymerization of styrene[13] and also in the γ-initiated polymerization of styrene.[34] It is thus expected that the γ-initiated emulsion polymerization of styrene mediated by PPPDTA should proceed via the RAFT mechanism without additional complications. NMR analyses of the products of the γ-initiated polymerization of styrene in the presence of PPPDTA were performed to verify that the appropriate products were obtained (including intermediate radical termination products), as described below.

Chain-Length-Dependent Termination. A crucial aspect of the interpretation of the data obtained here is chain-length-dependent termination. The termination reaction in free-radical polymerizations has been shown experimentally[35,36] and through theoretical arguments[26,37,38] to be controlled by the diffusion of the radical chain ends toward each other; in systems in which the polymer fraction is above c^* (the concentration at which chain overlap occurs), this process seems to be controlled by the center-of-mass diffusion of the parent chains, except at very high polymer fraction, when reaction–diffusion, caused by chain propagation, may take over.[26,39] Indeed, various experimental results have shown that CLD termination is necessary for the adequate interpretation of experimental data[35,40] and that termination in a classical (noncontrolled) emulsion polymerization (indeed, any conventional free-radical polymerization) is predominantly a short–long reaction between short radicals entering particles from the aqueous phase and/or generated by transfer to monomer.[40] It has been shown that the CLD termination reaction has a profound influence on the kinetics of RAFT-mediated polymerizations, in particular RAFT/emulsion systems.[20]

Including CLD termination in models of emulsion polymerization is difficult for two reasons.[20,41] First, termination rate coefficients that are valid at both nonzero weight fractions of polymer, w_p, and for chains of polymeric (not oligomeric) length are required. At present, the available models are either for quite short chain lengths, but high w_p,[42,43] or for polymeric chain lengths at vanishingly low w_p.[35,36,44] Unlike the quantitative interpretation needed for the present purposes, this is not particularly problematic for qualitative treatments, such as that presented previously,[20] as the important feature of the modeling was that termination had *some* chain-length dependence, not the specific details of the dependence. Second, the evolution equations describing the rate and molecular weight distribution, incorporating the compartmentalization of radicals into discrete particles, become extraordinarily complex except in the two limiting cases of zero–one and pseudo-bulk kinetics.[12] Thus, the "zero–one–two" evolution equations,[41] which should provide a quantitative description for systems not satisfying the conditions of either the zero–one and pseudo-bulk limits, involve coupled nonlinear partial integrodifferential equations in three independent variables and have, so far, only been solved under approximations that are inapplicable to controlled-radical systems.[45]

This situation becomes even more complex in a RAFT system because of the need to account for the chain-length distribution of dormant chains. While the two limits, zero–one and pseudo-bulk, are widely applicable in conventional emulsion polymerizations, this is not the case for RAFT systems,[20] and until recently, Monte Carlo simulations seemed to be the only method available to interpret data.[45] Apart from the very long computational times that this involves, such simulations do not provide simple means of extracting information such as rate coefficients through comparison to experiments (cf. the "slope–intercept" method,[12,24] which enables the rate coefficients for radical entry and exit to be extracted from the time evolution of conversion in conventional zero–one systems, with minimal model-based assumptions). However, the Monte Carlo simulations give the means of determining the probability of a radical terminating in a particle as a function of its chain length, as discussed for non-RAFT systems previously,[45] and this opens the way to prediction and interpretation of relaxation data.

The key qualitative results from the modeling work of Prescott[20] for RAFT/emulsion with a high-activity RAFT agent are now summarized. At low conversion, all dormant chains and the propagating radicals are short. Thus, termination in this system is a short–short reaction ($k_t^{\text{short-short}}$) and is faster than in the absence of the RAFT agent ($k_t^{\text{short-long}}$). As a consequence, the lifetime of the radical is reduced by the addition of the RAFT agent. If zero–one kinetics are applicable in a non-RAFT system, then they are also applicable in the RAFT-mediated system at low conversion.

At higher conversion, the dormant chains (and the propagating radicals) are longer; hence, radical lifetimes are increased by the addition of the RAFT agent. This is because the entering radical transfers rapidly to one of the longer dormant chains, creating a short dormant chain. Termination then requires either a long–long reaction, $k_t^{\text{long-long}}$, or transfer of radical activity back to the short dormant chain followed by short–long termination. Both long–long termination and transfer back to one specific dormant chain are less likely to occur than propagation, and so termination is diminished. The transfer of radical activity back to the shortest dormant chain (the dormant species resulting from the transfer of the entering z-mer), though only present in relatively low concentrations, is an important route to termination, occurring frequently in the case of high-activity RAFT agents.

A significant outcome of the Monte Carlo modeling[20] is that low-activity RAFT agents have little effect on the kinetics of emulsion polymerization, as the probability of transfer is so low as not to alter whether a system will follow zero−one kinetics. The effects of low-activity RAFT agents on emulsion polymerizations have been explained in terms of the surface activity of the RAFT agents used and the "frustrated entry" of oligomeric radicals.[33]

In a system that is under good RAFT control (i.e., a system where polymerization is mediated by a high-activity RAFT agent such as PPPDTA), the number-average molecular weight is given by

$$\bar{M}_{\mathrm{n}} = x\,\frac{m_{\mathrm{mon}}}{n_{\mathrm{RAFT}}} \tag{2}$$

where x is the fractional conversion, m_{mon} is the mass of monomer initially added to the system, and n_{RAFT} is the number of moles of RAFT agent added. The average length (degree of polymerization) of the dormant chains, $\bar{X}_{\mathrm{n,d}}$, is used as a measure of the progress of the reaction (in many instances, $\bar{X}_{\mathrm{n,d}}$ may be used as a measure of conversion normalized for the amount of RAFT agent initially added). For an interval 3 emulsion polymerization (i.e., in the absence of monomer droplets[12]) in the presence of a high-activity RAFT agent, $\bar{X}_{\mathrm{n,d}}$ is given by the same expression as in a bulk system.

Relaxations and Radical Exit. While measuring the conversion as a function of time allows $\bar{n}$ to be determined, it is not possible to obtain unambiguous mechanistic information on the emulsion polymerization process with the information available from such chemically initiated studies alone. A useful technique for obtaining unambiguous kinetic parameters is the γ-relaxation experiment, which has been extensively used with various monomers including styrene,[29,40,46] methyl methacrylate,[47] and vinyl esters,[48,49] as well as the RAFT-mediated polymerization of styrene using xanthates.[33] The strength of the γ-relaxation experiment is that the external source of radicals (i.e., the γ-induced decomposition of water into various radical species[50,51]) may be turned on or off at will, simply by introducing the sample into, or removing it from, the γ-source. Thus, γ-relaxation provides two steady-state values of $\bar{n}$ (in-source and out-of-source) as well as the rate of approach to the new steady state; the latter non-steady-state behavior provides the data most sensitive to radical loss. When out of the γ-source, the system is not necessarily without radical sources, however, as the autoinitiation or spontaneous generation of radicals is still seen with monomers such as styrene[52] and chlorobutadiene.[28]

The relaxation is dependent not only on the entry of new radicals to lead to termination but also on the movement of radicals between particles. Relaxations of the emulsion polymerization of styrene have been described as follows.[29,40,52] Transfer to monomer reactions generate small, mobile radicals that have the ability to exit from a particle and move from one particle to another. Upon reentry, the monomeric radical may either terminate with a radical, should there be a preexisting radical in the particle, or commence propagation. This process is illustrated in Figure 1.

The frequency of radical exit thus determines the time scale of the relaxation. Generalizing from this, a system that is highly uncompartmentalized due to the rapid exchange of radicals between particles (i.e., when k is quite large and there is complete reentry of exited radicals) will have faster relaxations than a system that has a slower exchange of radicals (i.e., a lower value of k).

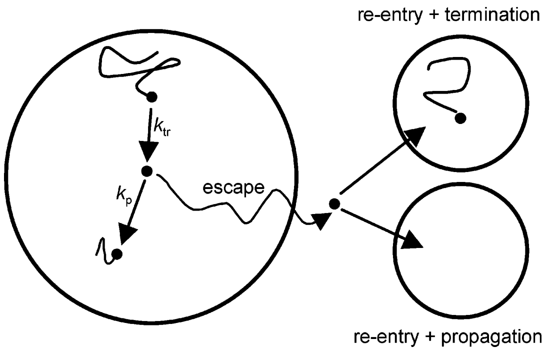


Figure 1. A schematic representation of the process by which the reduction in radical numbers occurs during a relaxation experiment in conventional emulsion polymerizations.

It may be noted that the rate coefficient for transfer to monomer should not be altered by the presence of a RAFT agent. Thus, the present level of understanding of RAFT/emulsion systems gives the expectation that a RAFT-mediated system that still follows zero−one kinetics (e.g., at low conversion with short dormant chains) would show relaxation kinetics similar to the equivalent non-RAFT system.

Adsorption and Desorption of Radicals. The Maxwell−Morrison model for radical entry[53] has been shown to agree with a large range of data (see van Berkel et al.[46] and references therein). It identifies the rate-determining step in the entry process as the propagation of the aqueous phase radicals to a length at which they may be considered to be surface active. This critical degree of polymerization for the radical to enter a particle is denoted z and, for reasonably hydrophobic monomers such as styrene with a water-soluble persulfate initiator, $z = 2{-}3$. This model has been successfully used to account for the entry efficiency in emulsion polymerization,[46,49,53,54] the homogeneous nucleation of new particles,[55−57] and the formation of core−shell particles.[57,58]

As a conceptual simplification, Maxwell et al.[53] suggested that a reasonable picture of the entry process was that a surface-active radical would enter the first particle with which it collided, although in Appendix B of their paper, they demonstrated that this assumption could be successfully relaxed with only minor quantitative effects. It was estimated that a z-meric styryl radical was much more likely to desorb from a particle than to enter it during an encounter; a z-mer would interact with the surface of many particles (of order 10^2, on average) before a propagation event occurred within one of these particles, then making the radical sufficiently water-insoluble as to be quite unlikely to desorb once more.

That the immediate and irreversible entry approximations are appropriate in many systems was demonstrated by comparing the frequency of desorption from a particle to the frequency of other fates for the radical, in particular aqueous phase propagation, aqueous phase termination, and particle-phase propagation.[53] However, the ability for a surface-active z-meric radical to desorb from one particle and move to another is quite significant for living polymerization systems in which the entering z-mer does not necessarily have to propagate to a $(z + 1)$-mer in order for radical activity to enter the particle; radical entry is thus reversible. This "RAFT-induced exit" mechanism is further developed here.

Theory

Monte Carlo Simulation of RAFT/Emulsion. The previously reported Monte Carlo modeling of radicals in RAFT-mediated emulsion polymerization[20] is extended here by a semiquantitative treatment of the previously reported results. The physical system described by the Monte Carlo modeling consists of a particle with a preexisting radical that has a new radical enter it from the aqueous phase. These two radicals may then undergo reactions, either propagating or terminating with each other (in a chain-length-dependent manner). The inclusion of dormant chains from the RAFT process provides a mechanism by which the length of the radical may change. The primary data obtained from the Monte Carlo model[20] are the probabilities P_j that j or more monomer units will be consumed in a two-radical environment before termination occurs.

For the purpose of later quantitative comparison with experiment, it is noted that the termination model used in the Monte Carlo simulations[20] was the diffusion model of Russell et al.[26,59] combined with an empirical scaling "law" developed by Griffiths et al.,[42,43] as follows:

$$k_{\mathrm{t}}^{ij} = 4\pi(D_i + D_j)p^{ij}\sigma N_{\mathrm{A}} \tag{3}$$

with

$$\frac{D_i(w_{\mathrm{p}})}{D_1(w_{\mathrm{p}})} = i^{-(0.664+2.02w_{\mathrm{p}})} \tag{4}$$

where σ is the distance at which two radical centers undergo termination (the position of the transition state, closely approximated by the van der Waals radius of monomer[60]) and $D_1(w_{\mathrm{p}})$ is the center-of-mass diffusion coefficient of monomer at polymer weight fraction w_{p}. (The full expression for this quantity given in the cited references has been simplified to take account of the conditions applicable to an emulsion polymerization.)

Semiquantitative Treatment of Monte Carlo Results. By looking at the average number of monomer units consumed in a test particle, $\overline{\Delta_{\mathrm{m}}}$, it is possible to obtain a value of c from the Monte Carlo simulation for a test particle initially containing two radicals:[45]

$$\overline{\Delta_{\mathrm{m}}} = \sum_{j\geq 0} P_j \tag{5}$$

$$\bar{c}(t) = \frac{k_{\mathrm{p}}C_{\mathrm{p}}}{\overline{\Delta_{\mathrm{m}}}} \tag{6}$$

where $\bar{c}(t)$ is a chain-length-independent average of contributions of the termination rate coefficients with appropriate weighting for the lengths of the radicals involved. While this would appear to provide a convenient method of interpreting the Monte Carlo results, evaluating $\overline{\Delta_{\mathrm{m}}}$ is fraught with difficulties due to limitations in the available CLD termination models.

An additional complication comes from the need to consider the number of chains that terminated as a function of the amount of monomer consumed; in situations where c is small, exceedingly large numbers of test particles must be considered to achieve a reasonable number of terminated chains (i.e., to obtain suitable precision from the simulation). A final difficulty is that $\overline{\Delta_{\mathrm{m}}}$ is an integral with an infinite upper bound. To achieve good convergence for $\overline{\Delta_{\mathrm{m}}}$ by direct integration of the model output, the minimum j that must be considered is often far in excess of what may be feasibly simulated.

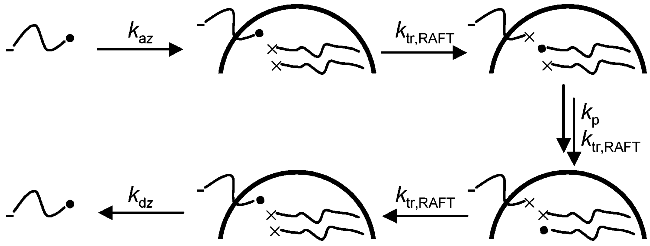


Figure 2. A schematic representation of the loss of compartmentalization through the regeneration of desorbing radicals from dormant z-meric RAFT-adducts. Symbols: radical, ●; dormant end group, ×.

Recognizing the above precautions and making suitable approximations, the model provides a semiquantitative measure of c, useful for understanding the effect of RAFT agents in changing the length of the propagating radicals.

Desorption of Oligomeric Radicals. The Maxwell–Morrison model for entry of radicals in an emulsion polymerization[53] will here to extended to account for the presence of the RAFT agent. In many systems, it is sufficient to assume that a z-meric radical enters irreversibly into the first particle it encounters.[53] This was shown by comparing the frequency of desorption from a particle to the time scale of other fates for the radical, in particular aqueous-phase propagation and termination.

However, in the case of a RAFT-mediated polymerization, the reaction that can cause the radical to enter the particle can be either propagation or transfer of radical activity to a dormant chain. This reaction leaves a z-meric-RAFT adduct $^{-}\mathrm{IM}_z{-}\mathrm{S}{-}\mathrm{C(Z)}{=}\mathrm{S}$ on the surface of the particle that is then able to be reactivated and possibly desorb later in the reaction. The probability of entry through formation of such a z-meric dormant species is high, with the probability of forming an adduct being given by

$$P(\text{form adduct}) = \frac{k_{\mathrm{tr,RAFT}}[\mathrm{RAFT}]}{k_{\mathrm{p}}[\mathrm{M}]_{\mathrm{p}} + k_{\mathrm{tr,RAFT}}[\mathrm{RAFT}]} \tag{7}$$

For a high-activity RAFT agent with transfer constant $C_{\mathrm{tr}} = 6000$ mediating the interval 2 polymerization of styrene at 50 °C (propagation rate coefficient[61] $k_{\mathrm{p}} = 2.4 \times 10^2\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, monomer concentration in the particles[12] $[\mathrm{M}]_{\mathrm{p}} = 5.5$ M) and $[\mathrm{RAFT}] = 8.5$ mM, P(form adduct) is 0.90. The formation of z-meric RAFT adducts is, thus, a significant process, not merely a marginal effect. For the purposes of this discussion, "z-meric RAFT adduct" refers only to the initiator-derived z-meric species, not $\mathrm{R}^{\bullet}$-derived chains (formed from the reinitiating group R) that have degree of polymerization z.

The z-meric RAFT adduct is water-insoluble to the extent that it is a surface-active species with a thiocabonylthio end group; hence, it will remain dormant on the surface of the particle until such time as it is reactivated via a transfer reaction. At that stage, the short radical so generated will have four possible fates: it may transfer activity to another RAFT agent, propagate, terminate with another radical (should there be one present in the particle), or desorb from the particle. As the z-mer is identical to the surface-active oligomeric radical that first entered the particle (which may have previously explored the surface of many particles), it is now free to leave that particle and explore the surface of other particles before repeating the same process.

This process is depicted pictorially in Figure 2 and may be formalized in the following scheme:

$$ {}^{-}\mathrm{IM}_z^{\bullet}(\mathrm{aq}) \underset{k_{\mathrm{d}z}}{\overset{k_{\mathrm{a}z}}{\rightleftharpoons}} {}^{-}\mathrm{IM}_z^{\bullet}(\mathrm{p}) \tag{8} $$

$$ {}^{-}\mathrm{IM}_z^{\bullet}(\mathrm{p}) + \mathrm{P}_n{-}\mathrm{X} \underset{k_{\mathrm{tr,RAFT}}}{\overset{k_{\mathrm{tr,RAFT}}}{\rightleftharpoons}} {}^{-}\mathrm{IM}_z{-}X(\mathrm{p}) + \mathrm{P}_n^{\bullet} \tag{9} $$

$$ \mathrm{P}_n^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \mathrm{P}_{n+1}^{\bullet} \tag{10} $$

where the state marking "(p)" denotes the particle phase, X denotes the thiocarbonylthio deactivating group, and $k_{\mathrm{a}z}$ and $k_{\mathrm{d}z}$ are the rate coefficients for the adsorption and desorption of the z-meric radical, respectively. Alternative pathways of propagation of the z-meric radical and termination with another radical are not shown in Figure 2 for simplicity.

In many ways, this process of transfer back to a dormant species followed by desorption is the same as transfer to monomer followed by exit of the monomeric radical. The overall effect of this is to decrease the compartmentalization of the system in the same way as addition of a highly active chain transfer agent, for example, can make a zero–one system progressively less compartmentalized until it becomes pseudo-bulk (k is increased until $k \gg c$). This phenomenon is described as a "RAFT-induced exit" mechanism.

In a γ-initiated system, the above mechanism must be reworked to use entering species[51] of $\mathrm{M}^{\bullet}$ and $\mathrm{HOM}^{\bullet}$ (where $\mathrm{HOM}^{\bullet}$ is the product of the addition of $\mathrm{HO}^{\bullet}$ across the vinyl group). These species have a water solubility similar to that of the monomer itself ($\mathrm{HOM}^{\bullet}$ being somewhat more soluble that M) and would, thus, be able to enter and exit from the particles in a manner similar to that described by Casey et al.[62] for the desorption of monomeric radicals formed by transfer to monomer reactions.

Estimating the rate coefficients for the adsorption and desorption processes in order to understand the importance of this effect is nontrivial. Using a Smoluchowski model for the adsorption rate coefficient, the following expression is obtained:[46,53]

$$ k_{\mathrm{a}z} = 4\pi D_z r_{\mathrm{s}} N_{\mathrm{A}} \tag{11} $$

where D_z is the diffusion coefficient for the z-mer and r_{s} is the swollen radius of the particle.

The desorption rate coefficient may be calculated from $k_{\mathrm{a}z}$ using microscopic reversibility if the free energy of adsorption is known; however, there are no such data available for the types of species of interest in the present study. Data from neutral arenes[63] and surfactant lability[64] must be used in place of more appropriate values, giving an order of magnitude estimate of $k_{\mathrm{d}z}$ $\sim 10^5$ s^{-1}.[53]

It is now possible to estimate the probability of the z-meric radical exiting a particle, $P(\text{exit-}z)$, once it is regenerated. An expression for $P(\text{exit-}z)$ may be developed in terms of the (pseudo-) first-order rate coefficients for the possible fates of the radical:

$$ P(\text{exit-}z) = \frac{k_{\mathrm{d}z}}{k_{\mathrm{d}z} + k_{\mathrm{p}}[\mathrm{M}]_{\mathrm{p}} + k_{\mathrm{tr,RAFT}}[\mathrm{RAFT}]} \tag{12} $$

The fate where the z-meric radical once again transfers is kinetically uninteresting (and there may be another opportunity for desorption at a later stage). In the case where another radical exists in the particle, termination may be trivially included in eq 12.

The rate coefficient for loss of a radical by exit from a particle, k, may now be estimated from this model, by combining the effect of transfer to monomer, followed by desorption of the monomeric radical, with transfer to z-meric RAFT adduct followed by desorption of the z-meric radical.

$$ k = k_{\mathrm{tr,RAFT}} C_z P(\text{exit-}z) + k_{\mathrm{tr}}[\mathrm{M}]_{\mathrm{p}} P(\text{exit-M}) \tag{13} $$

where C_z is the concentration of z-meric RAFT adduct in the particle and $P(\text{exit-M})$ is given by the usual expression

$$ P(\text{exit-M}) = \frac{k_{\mathrm{dM}}}{k_{\mathrm{dM}} + k_{\mathrm{p}}^{1}[\mathrm{M}]_{\mathrm{p}}} \tag{14} $$

The first-order rate coefficient for the desorption of the monomeric radical, k_{dM}, is expressed in terms of the diffusion coefficient and solubility of the monomer (assumed to be the same as those of the radical) in water, D_{w} and $[\mathrm{M}]_{\mathrm{w}}$:[65]

$$ k_{\mathrm{dM}} = \frac{3D_{\mathrm{w}}[\mathrm{M}]_{\mathrm{w}}}{r_{\mathrm{s}}^{2}[\mathrm{M}]_{\mathrm{p}}} \tag{15} $$

It is shown below that the effect of exit of z-meric radicals is, by far, the dominant factor in terms of radical loss processes, with transfer to monomer making a negligible contribution to k from eq 13 in the presence of a high-activity RAFT agent.

Using the RAFT-induced exit model described here, the rate coefficient for the exit of one radical from the particle, k, may be estimated using eq 13 and the parameters shown in Tables 1 and 2. This in turn may be compared to the value of c obtained from the relaxation experiments to determine the applicability of various kinetic models to the system. By way of comparison, Table 3 shows calculated values for k for an r_{s} = 50 nm particle in the persulfate-initiated emulsion polymerizations of styrene, methyl methacrylate (MMA), and butyl acrylate (BA) in the absence of RAFT as well as for a RAFT-containing styrene system with a high-activity RAFT agent (both persulfate- and γ-initiated). In the RAFT-containing case, it is assumed that there is only one z-meric RAFT adduct present in the particle, although it is conceivable that more would be present.

Table 3 illustrates that the presence of only one z-meric RAFT adduct in the particle is predicted to cause a 400-fold increase in the rate coefficient for radical loss from the particles in the case of a persulfate-initiated emulsion polymerization or a 40-fold increase in k for a γ-initiated polymerization. Moreover, k will scale linearly with the number of z-mer RAFT adducts in the particle, should more than one such adduct be present.

Given the uncertainty in $k_{\mathrm{d}z}$, a sensitivity analysis over the range of feasible values may be performed.

Table 1. Parameters Used in Modeling the Systems under Consideration at 50 °C

parameter	styrene	ref	BA	ref	MMA	ref
$[\mathrm{M}]_\mathrm{p}$/mol dm^{-3}	5.5	12	5.7	66	6.6	67
$[\mathrm{M}]_\mathrm{w}$/mol dm^{-3}	4.3×10^{-3}	12	6.4×10^{-3}	68	0.15	67
k_p/dm^3 mol^{-1} s^{-1}	2.36×10^{2}	69	2.33×10^{4}	70	6.47×10^{2}	71
k_p^1/dm^3 mol^{-1} s^{-1}	9.4×10^{2}	*a*	9.3×10^{4}	*a*	2.6×10^{3}	*a*
k_tr/dm^3 mol^{-1} s^{-1}	8.51×10^{-3}	72	1.55	66	7.53×10^{-3}	73
D_w/cm^2 s^{-1}	1.5×10^{-5}	74	1.5×10^{-5}	75	1.7×10^{-5}	74

[a] Taking $k_\mathrm{p} \approx 4k_\mathrm{p}^1$.[12]

Table 2. Additional Parameters Used in the Calculations Presented Here[a]

parameter	value
r_s/nm	50
$C_z = 1/N_\mathrm{A}V_\mathrm{s}$/mol dm^{-3}	3.2×10^{-6}
$k_{\mathrm{d}z}$/s^{-1}	10^5

[a] C_z is the concentration of the z-mer RAFT adduct, and $k_{\mathrm{d}z}$ is the desorption rate coefficient for a z-meric radical.

Table 3. Comparison of the Calculated Rate Coefficients for the Exit of Radicals from Particles, k, Using the Parameters in Tables 1 and 2 in a Persulfate-Initiated Emulsion Polymerization and a C_tr = 6000 RAFT Agent with [RAFT] = 8.5 mM Where Indicated

system	k/s^{-1}
styrene	1.0×10^{-2}
BA	3.4×10^{-2}
MMA	3.6×10^{-2}
styrene + RAFT (γ-initiator)	4.4×10^{-1}
styrene + RAFT	4.0

Increasing $k_{\mathrm{d}z}$ (e.g., to 10^6 s^{-1}) makes little difference to the calculated value of k, as P(exit-z) ≈ 1 already; decreasing $k_{\mathrm{d}z}$ to 10^4 s^{-1} makes only a factor of 2 difference in k (insignificant in the context of a 400-fold increase in k induced by the RAFT agent).

Approximate Model for Radical Loss. The Monte Carlo modeling of RAFT/emulsion systems[20] showed that once the dormant chains are no longer short, even a relatively small latex particle is able to support more than one radical within it; therefore, c is reduced. Moreover, the kinetics of the relaxation are those of an uncompartmentalized system with the rapid exchange of radicals through the RAFT-induced exit mechanism, as illustrated in Figure 3. The estimate for k (Table 3) suggests that there will be a rapid exchange of radicals between particles, i.e., zero−one−two kinetics are most applicable, with pseudo-bulk kinetics providing a reasonable approximation to them.[45]

The rapid exchange by RAFT-induced exit in this mechanism suggests a very simple treatment for radical loss at higher conversion: to assume that the rate-determining step at all except low conversion is entirely between two long chains and that the actual distribution of the degrees of polymerization of these chains may be approximated by assuming that this is instead monodisperse, with the appropriate degree of polymerization i from eq 2. The value of c is then readily found from eq 3, with $\langle k_\mathrm{t}\rangle = k_\mathrm{t}^{ii}$. One thus obtains

$$c \approx \frac{8\pi p_{ii} D_i \sigma}{V_\mathrm{s}} \tag{16}$$

If the chain-length distribution were indeed monodisperse, then eq 16 would give a lower bound to the exact value because it ignores short−long termination events (which will be faster than long−long ones); in actuality, this will not be an exact lower bound because RAFT does not produce a completely monodisperse distribution. Figure 4 shows the value of c so obtained, compared to those from the Monte Carlo calculation,[20] with the same parameters (all specified above; the parameter values for $[\mathrm{M}]_\mathrm{p}$ correspond to w_p = 0.39). It is apparent that

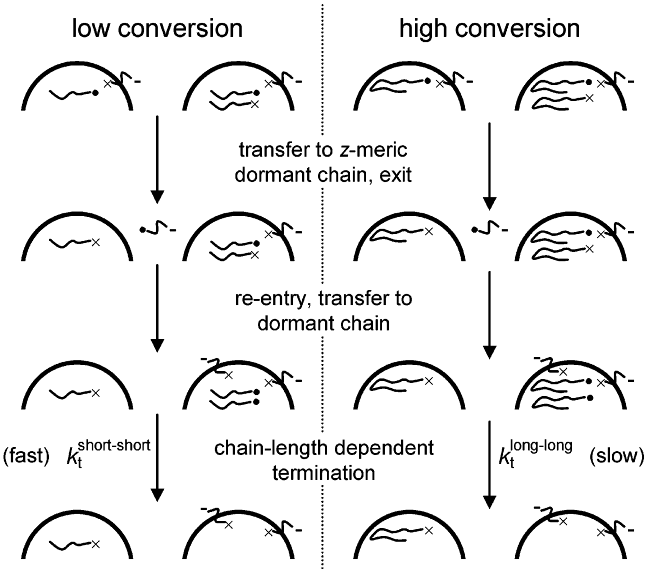


Figure 3. Relaxations in an uncompartmentalized RAFT-mediated emulsion polymerization are governed by short−short termination at low conversion and, later, by much slower termination reactions at higher conversion (most probable path shown). Symbols: radical, ●; dormant end group, ×.

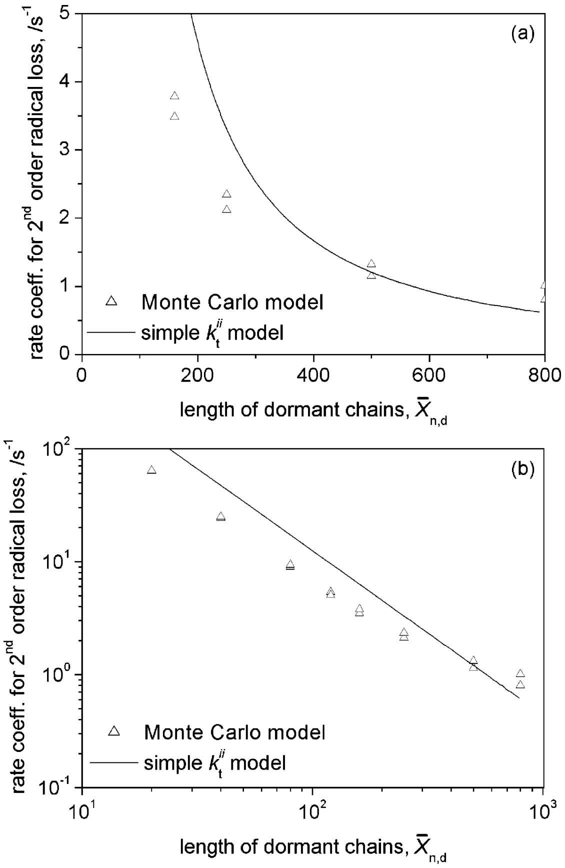


Figure 4. Value of c from Monte Carlo calculation (points) and from approximate formula of eq 16 (line) with the parameter values specified in the text; (a) and (b) are from the same data set with linear and logarithmic scales, respectively.

this simple approximate formula gives a good approximation to the "true" values from the Monte Carlo simulation, at least for higher conversion, corresponding to degrees of polymerization $\gtrsim 200$ for this particular parameter set.

Treatment of Dilatometry Data. Kinetic analysis of dilatometry data requires the application of an appropriate model for the evolution of $\bar{n}$ as a function of time. Cautiously drawing analogy to the equivalent non-RAFT system to the system studied in detail here, it is likely that all exited monomeric radicals would reenter another particle and propagate in that particle rather than reexiting.[12] Since zero−one kinetics are inappropriate and zero−one−two kinetics are troublesome for data analysis, here, we will use pseudo-bulk kinetics as an approximation to the full CLD zero−one−two model; an error of 10−20% in the rate of polymerization is to be expected from this assumption.[45] Application of pseudo-bulk kinetics gives the following expression for a relaxation (i.e., final $\bar{n}$ < initial $\bar{n}$):

$$\bar{n}(t) = \frac{\bar{n}_{\mathrm{sp}}}{\tanh\left(2\bar{n}_{\mathrm{sp}}ct + \tanh^{-1}\left(\frac{\bar{n}_{\mathrm{sp}}}{\bar{n}_{\mathrm{i}}}\right)\right)} \tag{17}$$

where $\bar{n}_{\mathrm{sp}}$ is the experimentally determined $\bar{n}$ due only to spontaneous initiation and $\bar{n}_{\mathrm{i}} = \bar{n}(t{=}0)$.

The appropriate data-processing procedure is to fit the conversion vs time data from the dilatometry experiment to the integrated form of the kinetics (eq 17). The use of a simplex algorithm to perform this curve fitting is quite appropriate and does not introduce significant noise or interdependencies between points through numerical differentiation nor overly weight the earliest-time points.

Experimental Section

Materials. Inhibitors were removed from the styrene using a commercial inhibitor removal column (Aldrich). Demineralized water was used throughout the experiments. All other materials were used as received from Aldrich. The RAFT agent PPPDTA was synthesized as previously reported.[13]

Radical Storage. PPPDTA was dissolved in styrene ([RAFT] = 12.9 mM) and thoroughly degassed through three freeze−thaw−evacuate cycles before being sealed under vacuum. Following the method of Barner-Kowollik et al.[19] for investigating radical storage in RAFT-mediated polymerizations, the ampules were subjected to γ-radiation for 18 h at ambient temperature using a 673 Gy h^{-1} ^{60}Co γ-cell. The samples were subsequently stored at room temperature for 20−60 min before being heated for 24 h at 50 °C in the absence of an external initiation source. Monomer conversion was determined by gravimetry and molecular weight distributions by GPC.

Seeded Emulsion Polymerization. A polystyrene latex was prepared as described by Prescott et al.,[13] giving a 25% solids latex with weight-average particle radius $\bar{r}_{\mathrm{w}} = 39$ nm, $\bar{r}_{\mathrm{w}}/\bar{r}_{\mathrm{n}} = 1.18$, particle number concentration $N_{\mathrm{p}} = 2.2 \times 10^{18}$ dm^{-3} (calculated from $\bar{r}_{\mathrm{n}}$, the number-average particle radius), molecular weight $\bar{M}_{\mathrm{n}} = 7.4 \times 10^4$, and $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} = 3.4$.

Styrene/polystyrene/PPPDTA seeds were prepared using the acetone transport technique described previously,[13] with varying in-particle concentrations of RAFT agent (at $[\mathrm{M}]_{\mathrm{p}} = [\mathrm{M}]_{\mathrm{p}}^{\mathrm{sat}}$) of [RAFT] = 0, 3.7, 8.5, 20, 27, and 38 mM. For the control experiments with [RAFT] = 0, the seeds were still subjected to the acetone transport technique, but without the RAFT agent. Determination of the conversion by gravimetry, particle size distribution, and molecular weight distribution was done as previously described.[13]

NMR Analyses. Ampules containing PPPDTA/styrene solution were prepared as described above with [RAFT] = 545 mM and irradiated for up to 32 h at 50 °C using a 673 Gy h^{-1} ^{60}Co γ-cell. Samples were dissolved in chloroform-*d* to give a solution volume of ~0.7 mL. The solutions were placed into 5 mm NMR tubes (Wilmad 535 or New Era UL5). For quantitative ^{13}C measurements, ~3% Cr(acac)$_3$ was added to the solution as the relaxation agent. The NMR spectra were acquired on a Bruker DRX500 spectrometer equipped with a 5 mm inverse *z*-gradient ^{1}H−^{13}C−^{15}N (TXI) probe operating at 500.13 MHz for ^{1}H and 125.6 MHz for ^{13}C. The temperature was controlled to 305 K. All experiments were acquired with Bruker standard pulse sequences. The samples were analyzed with ^{1}H, quantitative-^{13}C, COSY, HSQC, and HMBC experiments, the details of which are included in the Supporting Information.

Dilatometry. The dilatometry experiments were carried out in a jacketed glass vessel, approximately 30 cm^3 in volume. The temperature was controlled using a water bath. Each of the seed latex, monomer, and additional water were thoroughly degassed under vacuum, backfilling with argon. Monomer was added to the seed with stirring and allowed to swell the seed particles overnight under an argon blanket. The mixture was further degassed under vacuum and then brought to reaction temperature. Degassed water was added and the capillary topped up with decane. The particle number concentration, N_{p}, of the final latex was variously 1×10^{17} or 2×10^{17} dm^{-3}.

Once thermal equilibrium had been reached, the height of the meniscus in the capillary was followed using a computer-controlled tracking device. The dilatometer was lowered into a 151 Gy h^{-1} ^{60}Co γ-cell to initiate polymerization. A lead-encased lift mechanism that is capable of moving the auto-dilatometer and sample into the irradiation chamber is used.[11] Once the reaction appeared to have reached a constant rate of polymerization, the dilatometer was removed from the γ-source. Once the out-of-source steady state had been reached, the dilatometer was reinserted into the γ-source, and the relaxation procedure was repeated up to eight times.

Rate data were extracted from the meniscus height data using the densities for styrene and polystyrene from Hawkett et al.[24,52] The small correction required at low conversion to account for the changing length of the chains was not applied, as this requires a second, independent method by which conversion may be measured to determine the required correction. The low conversion data are not used in the analyses presented here because pseudo-bulk kinetics are in appropriate, as discussed above.

Results and Discussion

Radical Storage. Whereas the original radical storage experiments of Barner-Kowollik et al.[19] showed a significant difference in the conversion of the RAFT and non-RAFT samples both after irradiation and after heating to polymerization temperature, the same was not observed for the corresponding experiments performed here with PPPDTA, a benzyl-activated RAFT agent, as illustrated in Figure 5. We conclude from these data that no radical storage mechanism is operative in this system. Note that the γ-source used in the present study has a higher dose rate than that used by Barner-Kowollik et al.[19] The conversion of each sample is thus not directly comparable, but it is only the *difference* in conversion between the RAFT and non-RAFT samples that is of interest in analyzing these data.

This result is consistent with the experiments of Barner-Kowollik et al.,[19] as the intermediate bipolymeric radical formed by phenyl-activated RAFT agents (e.g., CDTB) is much more stable than that formed by the benzyl-activated RAFT agent (PPPDTA). The less stable intermediate will have a shorter lifetime;[19] hence, it will be present in lower concentrations and will be less able to take part in reactions, such as termination reactions, with other species.[76] The radical storage

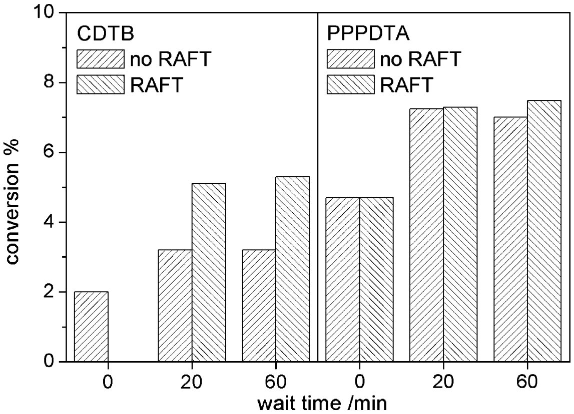


Figure 5. Conversion of different samples with the RAFT agent PPPDTA obtained here compared to the results for CDTB of Barner-Kowollik et al.[19] The difference in conversion between the RAFT and non-RAFT samples that was observed by Barner-Kowollik et al.[19] for their phenyl-activated RAFT agent was not observed with the present benzyl-activated RAFT agent.

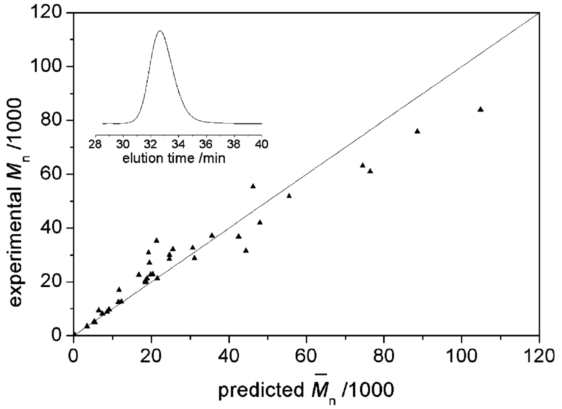


Figure 6. Calculated and experimentally determined value of $\bar{M}_n$ for a variety of γ-initiated experiments including sealed ampules and emulsion polymerization experiments, showing good control of molecular weight over the range $\bar{M}_n = 5 \times 10^2$ to 1×10^5. Inset: a typical raw GPC chromatogram. For all samples, $1.1 < \bar{M}_w/\bar{M}_n < 1.4$.

effects attributed by Barner-Kowollik et al.[19] to reactions of the intermediate radical are thus less likely to occur in PPPDTA-mediated polymerizations, as observed here.

In the NMR analyses performed in this study, the major products observed were the RAFT-containing chain formed from the cumyl reinitiating group with an average of 2.1 styrene units in the polymer backbone. No evidence of an intermediate radical termination product was observed in the spectra, with all signals in the region where the quaternary carbon of the coupling product is expected to be found being assigned to other groups (more details are in the Supporting Information). It is noted that formation of intermediate termination products at levels that could not be detected by these experiments may be kinetically significant; however, these experiments set an upper bound on the levels of termination products that can be observed in the case of an experiment that was designed to lead to the formation of such species.

Molecular Weight Control. The molecular weight of the polymer produced in a large number of reactions is shown in Figure 6. In each case, γ-initiation was used, with the dose rate varying between 75 and 673 Gy h^{-1}. Samples from both bulk and emulsion polymerizations are included, with the emulsion polymer results covering a range of [RAFT] and final conversions. In each case, the theoretical value of $\bar{M}_n$ is calculated using eq 2.

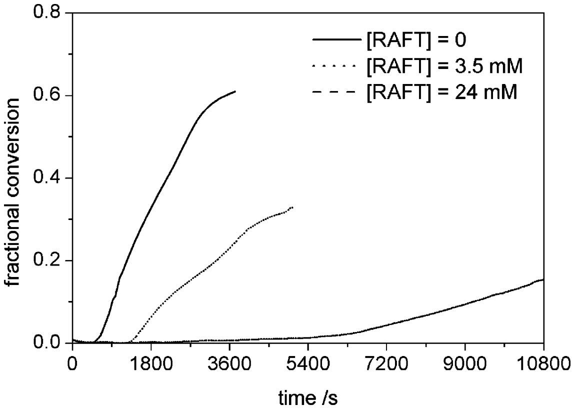


Figure 7. Conversion vs time for the emulsion polymerization of styrene at [RAFT] = 0, 3.5, and 24 mM. Each system was started at the interval 2/3 transition with $N_p = 2 \times 10^{17}$ dm^{-3}, $r_s = 48$ nm, 151 Gy h^{-1} γ-source.

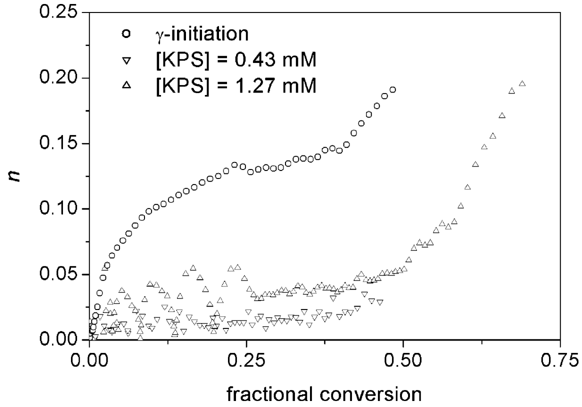


Figure 8. Experimental $\bar{n}$ as a function of time for RAFT/emulsion systems with various initiation systems and [RAFT]. For persulfate (KPS) initiation, [PPPDTA] = 60 mM and for γ-initiation, [PPPDTA] = 25 mM. These data, showing $\bar{n}$ increasing over time in intervals 2 and 3, are inconsistent with zero−one kinetics for the systems under consideration.

Rate of Polymerization. In RAFT-mediated polymerizations, a reduction in the rate of polymerization is often observed,[16,77,78] and both chemically- and γ-initiated RAFT/emulsion systems are no exception.[13,33] Figure 7 shows the conversion vs time plots for three emulsion polymerizations, [RAFT] being the only difference between them. As previously seen in the chemically initiated studies,[13] the rate of polymerization is reduced by the addition of the RAFT agent, and the strength of this effect is dependent on how much RAFT agent is added.

Noting that these experiments were conducted in interval 3 (i.e., no monomer droplets present); $[M]_p$ is monotonically decreasing throughout the course of the reaction. As a result, $\bar{n}$ is increasing with conversion, as shown in Figure 8. It is generally understood that $\bar{n}$ should remain constant throughout the polymerization in a zero−one system because changes in the viscosity of the particle do not change the basic kinetic parameters (termination is "pseudo-instantaneous"[24] and radical desorption depends on aqueous phase, not in-particle diffusion rates[65]). That $\bar{n}$ increases in Figure 8 indicates that the systems are not behaving in a zero−one manner; this is consistent with the modeling results[20]

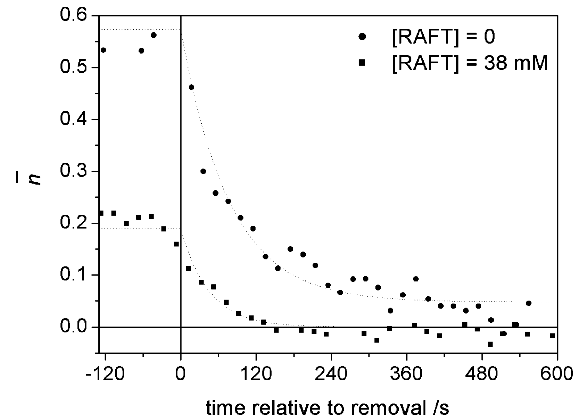


Figure 9. Sample relaxation data ($\bar{n}$ vs time) showing the effect of the RAFT agent. The average shown for the in-source n is the average over the previous 500 s, with the sample removed from the γ-source at time $t = 0$. Both the in-source and out-of source n are reduced by the addition of the RAFT agent.

that indicated that RAFT/emulsion systems with high-activity RAFT agents would not be zero−one except when the dormant chains are quite short. These data are also inconsistent with the simple application of zero−one kinetics in that zero−one kinetics cannot account for the reduction in the rate of polymerization induced by the addition of the RAFT agent to the system.[13]

Relaxations. For the emulsion polymerization of styrene with PPPDTA, γ-radiolysis experiments showed that the cessation of initiation leads to a rapid decrease in the rate of polymerization, with polymerization effectively ceasing 100−200 s after irradiation was stopped. Representative relaxation data ($\bar{n}$ vs time) are shown in Figure 9; it is seen that both the in-source and out-of-source steady-state values for $\bar{n}$ are reduced by the addition of the RAFT agent as well as the characteristic time scale of the relaxation. (That $\bar{n}$ slightly exceeds 0.5 in the non-RAFT data shown in Figure 9 is probably an artifact arising from a slight error in N_p due to uncertainty in the particle size.)

As discussed above, the chain-length dependence of termination is important in correctly describing RAFT/emulsion systems, and the chain length of the radicals is determined by the (average) chain length of the dormant chains, $\bar{X}_{n,d}$. A pseudo-bulk kinetics treatment of the relaxation data at various conversions, [RAFT], $[M]_p$, and N_p is shown in Figure 10, with $\bar{X}_{n,d}$ calculated from eq 2.

The relaxation behavior shown in Figure 10 is dependent on the length of the dormant chains in the system, over a wide range of experimental conditions. When the system is sufficiently uncompartmentalized that pseudo-bulk kinetics provide an adequate description, the rate coefficient for second-order radical loss shown in Figure 10 is the parameter c; when the system is zero−one (limit 2a), the second-order radical loss is given by $k = k_{tr}[M]_p k_{dM}/(k_p^1[M]_p + k_{dM})$ and is not directly related to termination.[12,62] In this system, pseudo-bulk kinetics are a reasonable approximation for $\bar{X}_{n,d} \gtrsim 40$, at which point termination is sufficiently slowed to allow significant amounts of polymer to be produced in a two-radical environment.[20] Thus, for the longer dormant chain lengths, the average value of the second-order termination rate coefficient, $\langle k_t \rangle$, may be extracted from the data presented in Figure 10 using the relation $c = \langle k_t \rangle / N_A V_s$, as shown in Figure 11.

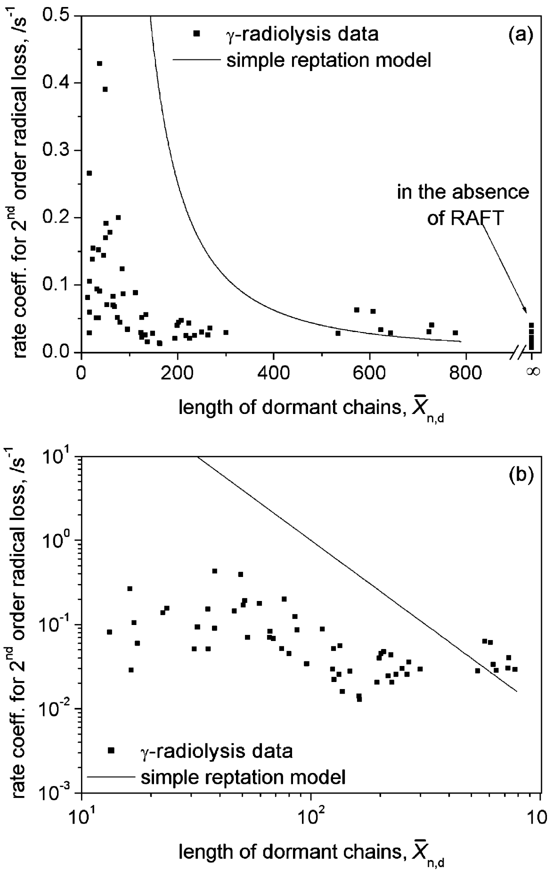


Figure 10. Rate coefficients for radical loss, c, from experiment (■) and calculated using a simple reptation model (—). The values of c are only accurate for long dormant chains (i.e., $\bar{X}_{n,d} \gtrsim 40$). Panels (a) and (b) are from the same data set on a linear and log scale, respectively.

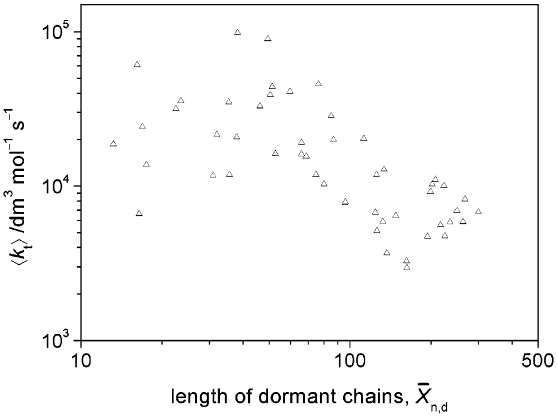


Figure 11. Value of $\langle k_t \rangle$ as a function of the dormant chain length $\bar{X}_{n,d}$. Note that, where the system is not described by pseudo-bulk kinetics (i.e., $\bar{X}_{n,d} \lesssim 40$), the rate coefficient for second-order radical loss is not c and the value shown here is not $\langle k_t \rangle$.

Prediction of Relaxation Behavior. The integral technique previously described for the semiquantitative treatment of the Monte Carlo results may be used to calculate values of c.[45] It is apparent on comparison of these predictions, given as points in Figure 4, to the data of Figure 10 that these calculations are incorrect by about a factor of about 50, although the general shape of the experimental results is the same as this prediction.

Now, the Monte Carlo calculation used a model for CLD termination, eq 4, that could be seen as inappropriate as it is extrapolated from 5 (the highest degree of polymerization for the styrene data in the results for styrene, BMA, HEMA, and MMA used to infer eq 4) to hundreds of units. The data for $\langle k_t \rangle$ shown in Figure 11 could, in principle, be improved through more experiments to show the variation of $\langle k_t \rangle$ with both w_p and $\bar{X}_{n,d}$ in a manner similar to Vana et al.[79]

Although data for this chain-length dependence are not yet available, a more physically reasonable scaling for longer chains in the presence of large amounts of polymer (i.e., at the weight fraction of polymer of 0.39 for the present system) than provided by eq 4 (only tested for chains of degree of polymerization 5 and less for styrene) would be the scaling predicted by reptation, viz., an exponent of 2. That is, one replaces the scaling of eq 4 by

$$\frac{D_i(w_p)}{D_1(w_p)} = i^{-2} \tag{18}$$

The results of using this exponent in the approximate expression for c given by eq 16 are compared with experiment in Figure 10. There is good agreement between this model and the data for the longer chain lengths. The observation that this simple model also reproduces corresponding Monte Carlo simulation data at longer chain lengths (Figure 4) suggests that this accord between the theoretical and experimental dependence of c on length of the dormant chain shown in Figure 10 is a strong indicator of the importance of CLD termination in describing the system. The differences between the experimental data set and the predicted values of c are to be expected given the difficulties in preparing theoretical values of c and the inapplicability of pseudo-bulk kinetics to the zero−one system at lower $\bar{X}_{n,d}$.

The data interpretation given above is consistent with the dominant loss mechanism being termination between two long radicals growing under RAFT control. Note the non-RAFT value for c in Figure 10 was obtained by fitting the relaxation data to *pseudo-bulk* kinetics; however, it has been established that this non-RAFT system follows *zero−one* kinetics. While interesting, the trend of the RAFT data to this value may be coincidental.

Conclusions

It has been shown here that the γ-initiated polymerization of styrene may be successfully mediated by the benzyl-activated RAFT agent PPPDTA. Good control over the molecular weight of the products was shown. NMR analyses of the products of γ-initiated polymerizations did not detect any intermediate radical coupling species and radical storage effects were not observed. Retardation of the rate of polymerization was observed with an increase in [RAFT]. In the emulsion polymerization of styrene, an increase in $\bar{n}$ with conversion was seen, indicating that zero−one kinetics are inappropriate for these systems except, perhaps, at low conversions.

The presence of z-meric dormant chains in the particles was postulated to lead to an increase in the rate of radical exit from the particles, since z-meric radicals are able to desorb from the particle surface. This RAFT-induced exit mechanism leads to radical entry being a reversible process and a rapid exchange of radicals between particles, with the rate coefficient for radical desorption from a particle being increased by ~400-fold. The time-dependent behavior of the number of z-meric dormant species is, thus, an important subject for further study.

A semiquantitative treatment of Monte Carlo simulations describing this mechanism was seen to give a good description of the shape of the relationship between c and the length of the dormant chains. Moreover, these simulations and modeling of radical exit suggest that in RAFT emulsion systems the rate-determining step for radical loss is the termination between two long radicals. A simple reptation model gives quantitative accord with the computationally expensive Monte Carlo simulations for longer chain lengths. This supports the applicability of the qualitative explanations given here for the origins of the strong effect of RAFT on γ-relaxations.

Kinetic parameters were obtained from the γ-relaxation experiments, making use of both Monte Carlo modeling of RAFT/emulsion particles and the RAFT-induced exit mechanism for the rapid exchange of radicals between particles to justify the use of pseudo-bulk kinetics for these systems. The use of pseudo-bulk kinetics permitted the determination of $\langle k_t \rangle$ as a function of the dormant chain length, offering a method whereby k_t^{ii} may be determined at both high w_p and chain lengths.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Müller, A. H. E.; Zhuang, R.; Yan, D.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326−4333.
(2) Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001.
(3) Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365−375.
(4) Vosloo, J. J.; De Wet-Roos, D.; Tonge, M. P.; Sanderson, R. D. *Macromolecules* **2002**, *35*, 4894−4902.
(5) Moad, G.; Rizzardo, E.; Solomon, D. H.; Beckwith, A. L. J. *Polym. Bull. (Berlin)* **1992**, *29*, 647−652.
(6) Matyjaszewski, K. *Chem.*−*Eur. J.* **1999**, *5*, 3095−3102.
(7) Matyjaszewski, K.; Patten, T. E.; Xia, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 674−680.

(8) Goto, A.; Ohno, K.; Fukuda, T. *Macromolecules* **1998**, *31*, 2809−2814.
(9) Matyjaszewski, K. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 769−776.
(10) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.
(11) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Aust. J. Chem.* **2002**, *55*, 415−424.
(12) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, 1995.
(13) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 5417−5425.
(14) Ferguson, C. J.; Hughes, R. J.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2002**, *35*, 9243−9245.
(15) Ferguson, C. J.; Hughes, R. J.; Nguyen, D.; Pham, B. T. T.; Hawkett, B. S.; Gilbert, R. G.; Serelis, A. K.; Such, C. H. *Macromolecules* **2005**, *38*, 2191−2204.
(16) Barner-Kowollik, C.; Quinn, J. F.; Nguyen, T. L. U.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2001**, *34*, 7849−7857.
(17) Barner-Kowollik, C.; Quinn, J. F.; Morsley, D. R.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1353−1365.
(18) Coote, M. L.; Radom, L. *J. Am. Chem. Soc.* **2003**, *125*, 1490−1491.
(19) Barner-Kowollik, C.; Vana, P.; Quinn, J. F.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1058−1063.
(20) Prescott, S. W. *Macromolecules* **2003**, *36*, 9608−9621.
(21) Wang, A. R.; Zhu, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1553−1566.
(22) Barner-Kowollik, C.; Coote, M. L.; Davis, T. P.; Radom, L.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2828−2832.
(23) Wang, A. R.; Zhu, S.; Kwak, Y.; Goto, A.; Fukuda, T.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2833−2839.
(24) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1323−1343.
(25) Ballard, M. J.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 533−537.
(26) Russell, G. T. *Aust. J. Chem.* **2002**, *55*, 399−414.
(27) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592−599.
(28) Christie, D. I.; Gilbert, R. G.; Congalidis, J. P.; Richards, J. R.; McMinn, J. H. *Macromolecules* **2001**, *34*, 5158−5168.
(29) Lansdowne, S. W.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1344−1355.
(30) Hong, C. Y.; You, Y. Z.; Bai, R. K.; Pan, C. Y.; Borjihan, G. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3934−3939.
(31) Quinn, J. F.; Barner, L.; Davis, T. P.; Thang, S. H.; Rizzardo, E. *Macromol. Rapid Commun.* **2002**, *23*, 717−721.
(32) Quinn, J. F.; Barner, L.; Rizzardo, E.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 19−25.
(33) Smulders, W.; Gilbert, R. G.; Monteiro, M. J. *Macromolecules* **2003**, *36*, 4309−4318.
(34) Barner, L.; Zwaneveld, N.; Perera, S.; Pham, Y.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4180−4192.
(35) de Kock, J. B. L.; Klumperman, B.; van Herk, A. M.; German, A. L. *Macromolecules* **1997**, *30*, 6743−6753.
(36) de Kock, J. B. L.; van Herk, A. M.; German, A. L. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 199−252.
(37) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935−940.
(38) Russell, G. T. *Macromol. Theory Simul* **1994**, *3*, 439−468.
(39) Schulz, G. V. *Z. Phys. Chem. (Frankfurt am Main)* **1956**, *8*, 290−317.
(40) Adams, M. E.; Russell, G. T.; Casey, B. S.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624−4634.
(41) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552−569.
(42) Griffiths, M. C.; Strauch, J.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 7835−7844.
(43) Strauch, J.; McDonald, J.; Chapman, B. E.; Kuchel, P. W.; Hawkett, B. S.; Roberts, G. E.; Tonge, M. P.; Gilbert, R. G. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2491−2501.
(44) Smith, G. B.; Russell, G. T.; Heuts, J. P. A. *Macromol. Theory Simul.* **2003**, *12*, 299−314.
(45) Prescott, S. W.; Ballard, M. J.; Gilbert, R. G. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1076−1089.
(46) van Berkel, K. Y.; Russell, G. T.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 3921−3931.
(47) Ballard, M. J.; Napper, D. H.; Gilbert, R. G.; Sangster, D. F. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1027−1041.
(48) De Bruyn, H.; Gilbert, R. G.; Ballard, M. J. *Macromolecules* **1996**, *29*, 8666−8669.
(49) De Bruyn, H.; Miller, C. M.; Bassett, D. R.; Gilbert, R. G. *Macromolecules* **2002**, *35*, 8371−8377.
(50) McAskill, N. A.; Sangster, D. F. *Aust. J. Chem.* **1979**, *32*, 2611−2615.
(51) McAskill, N. A.; Sangster, D. F. *Aust. J. Chem.* **1984**, *37*, 2137−2143.
(52) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2395−2404.
(53) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629−1640.
(54) Vorwerg, L.; Gilbert, R. G. *Macromolecules* **2000**, *33*, 6693−6703.
(55) Morrison, B. R.; Maxwell, I. A.; Gilbert, R. G.; Napper, D. H. In *ACS Symposium Series; Polymer Latexes—Preparation, Characterization and Applications*; Daniels, E. S., Sudol, E. D., El-Aasser, M., Eds.; American Chemical Society: Washington, DC, 1992; Vol. 492.
(56) Prescott, S. W.; Fellows, C. M.; Gilbert, R. G. *Macromol. Theory Simul.* **2002**, *11*, 163−170.
(57) Ferguson, C. J.; Russell, G. T.; Gilbert, R. G. *Polymer* **2002**, *43*, 4557−4570.
(58) Ferguson, C. J.; Russell, G. T.; Gilbert, R. G. *Polymer* **2002**, *43*, 6371−6382.
(59) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 2459−2469.
(60) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2133-2140.
(61) Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 293−297.
(62) Casey, B. S.; Morrison, B. R.; Maxwell, I. A.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 605−630.
(63) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279−291.
(64) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielman, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, *80*, 905−922.
(65) Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol.* **1976**, *49*, 536−609.
(66) Maeder, S.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 4410−4418.
(67) Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3225−3253.
(68) Capek, I.; Barton, J.; Ordinova, E. *Chem. Zvesti* **1984**, *38*, 803−822.
(69) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267−3280.
(70) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206−4215.
(71) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiwara, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, *201*, 1355−1364.
(72) Tobolsky, A. V.; Offenbach, J. *J. Polym. Sci.* **1955**, *16*, 311−314.
(73) Whang, B. C. Y.; Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *Aust. J. Chem.* **1991**, *44*, 1133−1137.
(74) Wilke, C. R.; Chang, P. *AIChE J.* **1955**, *1*, 264−270.
(75) Immanuel, C. D.; Cordeiro, C. F.; Sundaram, S. S.; Meadows, E. S.; Crowley, T. J.; Doyle, F. J., III *Comput. Chem. Eng.* **2002**, *26*, 1133−1152.
(76) Kwak, Y.; Goto, A.; Tsujii, Y.; Murata, Y.; Komatsu, K.; Fukuda, T. *Macromolecules* **2002**, *35*, 3026−3029.
(77) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283.
(78) Chong, B. Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.
(79) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2002**, *23*, 952−956.

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