Effects of Reversible Addition Fragmentation Transfer (RAFT) on Branching in Vinyl Acetate Bulk Polymerization[†]

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A detailed mathematical model has been formulated for branching due to chain transfer to polymer in reversible addition fragmentation chain transfer (RAFT) polymerization. The traditionally adopted mechanism for RAFT polymerization has been modified by the inclusion of a relaxation process. It is proposed that this step occurs during the period immediately after a chain radical is released from the RAFT transfer intermediate. While undergoing relaxation, the so-called unrelaxed radicals are assumed to be capable of propagation, intermolecular chain transfer to polymer, and bimolecular termination, but not intramolecular chain transfer to polymer which only becomes possible when the radical is relaxed. The use of these assumptions indicates that RAFT can reduce the overall rate of branching without significantly affecting other key measurements such as conversion and average molecular weights. If relaxation is neglected, RAFT would appear not to affect the rate of branching. However, by reducing the average molecular weight, RAFT polymerization would still result in more linear polymers as compared to conventional methods.

1. Introduction

Reversible addition fragmentation transfer (RAFT) is increasingly being adopted as an efficient and effective method to control polymerization. RAFT has several advantages over conventional free-radical polymerization. It permits good control of molecular weights and polydispersities[1] and allows block polymers to be created with relative ease.[2] It has been successfully applied to a wide range of systems including bulk,[3] solution,[4] emulsion,[5] and miniemulsion[6] polymerizations. Further, RAFT polymerization has been used to create novel products including nanoparticles[7] and star polymers.[8]

The mechanism of RAFT polymerization has been the focus of much attention. It is generally accepted that the exchange process involves two steps.[9−18] In the first step, a polymer chain with an attached RAFT molecule combines with a second polymer chain with an available radical to form an intermediate radical species. This intermediate then undergoes fragmentation resulting in transfer of the RAFT agent from one polymer chain to the other. This mechanism has been studied in considerable detail.[15] However, there is still some uncertainty regarding some aspects, particularly the rate of fragmentation of the intermediate.[19,20]

One important aspect that appears to have been overlooked in modeling of RAFT polymerization is the effects of chain transfer to polymer which leads to branching, though several models of branching in polymerization are available in the literature.[21−28] Chain transfer to polymer is known to make important contributions in free-radical polymerizations of several monomers, in particular ethylene,[29−37] vinyl acetate,[38−43] and acrylates.[42−49] There is now firm evidence that chain transfer to polymer takes place in RAFT polymerizations of acrylic acid[50] and acrylates,[51] so it is relevant to include such processes when modeling RAFT polymerizations. In this paper, a detailed mathematical model of RAFT polymerization is formulated. The proposed model employs a modified kinetics scheme as compared to the scheme employed in the studies previously mentioned. The need for this scheme is demonstrated in the first instance by theoretical inspection of a simple model of branching in RAFT polymerization. Then, employing the

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detailed model formulated below, numerical studies have been undertaken demonstrating the effectiveness of the proposed mechanism in providing one possible explanation for the observed reduction in branching in RAFT polymerization.[51]

2. Model Development

2.1. Proposed Mechanism for RAFT Transfer. The transfer of a RAFT agent from one polymer chain to another is traditionally modeled by the following set of two reversible reactions:[9,11−15]

$$P_1^* + \hat{P}_2 \rightleftharpoons P_1^*\hat{P}_2 \rightleftharpoons \hat{P}_1 + P_2^* \tag{1}$$
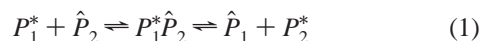
Here P_i^* represents a polymer chain with an uncapped radical, $\hat{P}_j$ represents a polymer chain with a radical capped with the RAFT agent, and $P_1^*\hat{P}_2$ represents an intermediate complex formed by interaction between the two polymer molecules. Some studies have also employed a pair of irreversible reactions with equal success:[10,16−18]

$$P_1^* + \hat{P}_2 \rightarrow P_1^*\hat{P}_2 \rightarrow \hat{P}_1 + P_2^* \tag{2}$$
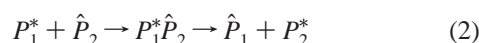
This mechanism has been used successfully in theoretical studies to explain experimentally observed phenomena such as the reduction of polydispersity in RAFT polymerization.[17] Additionally, it has been proposed that the intermediate $P_1^*\hat{P}_2$ is capable of undergoing reversible and irreversible bimolecular termination reactions with other radicals in the system.[52−54] Finally, a reduction in conversion in the presence of RAFT agents has been attributed to the stability of the intermediate $P_1^*\hat{P}_2$.[55]

Recent studies have shown that RAFT polymerization of butyl acrylate produces polymer with lower levels of branching than that from conventional free-radical polymerization.[51] As will be shown subsequently, use of the mechanism represented by eq 2 enables the prediction of key traits of RAFT polymerization— a linear increase in the number average molecular weight with conversion and a reduction in polydispersity—but does not indicate that RAFT polymerization has any effect on the branching characteristics of the polymer chains. This can also be shown mathematically, as discussed in Appendix A. Given that, for polymerization of ethylene, intramolecular chain transfer to polymer is well-known to be far more frequent than intermolecular chain transfer to polymer, it is reasonable to assume the same occurs in radical polymerizations of other monomers. On this basis, the specific chain-end conformation required for the intramolecular (so-called *back-biting*) reaction needs to be considered. In conventional free-radical polymerization, the chain end will have no restrictions on its conformation between additions of monomer. However, in RAFT polymerization, the chain radical is released from the RAFT transfer intermediate, i.e., from an attached group of substantial size, in which case the time scale for rearrangement of the chain end into its "normal" state of conformational freedom may be a factor that limits intramolecular chain transfer to polymer for a period immediately after the chain radical is released. Such radicals with initially constrained conformations would still be expected to undergo propagation and intermolecular chain transfer to polymer in the normal way (since they do not require specific chain-end conformations), so only short-chain branching would be reduced and not the long-chain branching that results from intermolecular chain transfer to polymer. On the basis of this hypothesis, the mechanism represented by eq 2 was modified by introducing a

"relaxation" step and a new type of radical called the unrelaxed radical:

$$P_1^* + \hat{P}_2 \rightarrow P_1^*\hat{P}_2 \rightarrow \hat{P}_1 + \tilde{P}_2 \rightarrow \hat{P}_1 + P_2^* \tag{3}$$
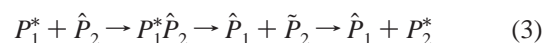
Here, $\tilde{P}_2$ represents a polymer chain with an unrelaxed radical attached to it.

Unrelaxed radicals are assumed to be formed at the instant when the RAFT agent leaves a polymer chain during the RAFT transfer process. These unrelaxed radicals are deemed capable of undergoing bimolecular termination reactions. However, a key difference between the mechanism described above and that presented here is that unrelaxed radicals are deemed capable of participating in propagation, termination, and intermolecular chain transfer reactions but not in intramolecular chain transfer to polymer. After a certain period (called "the relaxation time"), this unrelaxed radical is transformed into an active radical that can participate in all reactions. As discussed below, the introduction of unrelaxed radicals and long relaxation times can explain the observed effects of RAFT on branching without significantly altering the other effects of RAFT, namely, a linear increase in the number average molecular weight with conversion and a reduction in polydispersity.

2.2. Notation. In developing the reaction scheme, polymer chains were assumed to be differentiated by five characteristics, namely, the number of repeat units, branches, active radicals, inactive (capped) radicals, and unrelaxed (just uncapped) radicals. Using this assumption, polymer chains are denoted by P_{ijklm} where each index corresponds to one of the characteristics mentioned above. Specifically,

  i represents the number of repeat units,
  j represents the number of branches,
  k represents the number of active (uncapped) radicals,
  l represents the number of inactive (capped) radicals, and
  m represents the number of unrelaxed (just uncapped) radicals.

This notation was adopted in order to model the proposed kinetics scheme accurately and so that certain desirable measurements could be obtained. It should be noted that not all combinations of the indices are possible. In particular,

(1) the number of active, inactive, and unrelaxed radicals can each never exceed the number of repeat units in the polymer chain, i.e., $k, l, m \leq i \ \forall \ i, k, l, m$;

(2) the number of branches can never exceed the number of repeat units in the polymer chain, i.e., $j \leq i \ \forall \ i, j$; and

(3) the sum of the number of active, inactive, and unrelaxed radicals can never exceed the number of branches plus one (because a linear polymer has no branches but can still have an attached radical), i.e., $(k + l + m) \leq j + 1 \ \forall \ j, k, l, m$.

2.3. Reaction Scheme. In order to keep the model simple, only a few key reactions were considered. For example, chain transfer to monomer was neglected as was varying initiator efficiency. Termination by disproportionation was neglected as it was found to be negligible in vinyl acetate polymerization. Thus, the following reaction scheme was formulated for use in this study.
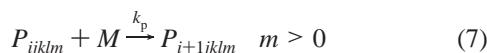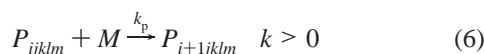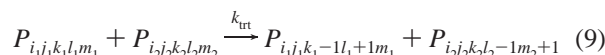
Initiator decomposition

$$I \xrightarrow{k_d} 2R \tag{4}$$

Initiation

$$R + M \xrightarrow{k_i} P_{10100} \tag{5}$$

Propagation

$$P_{ijklm} + M \xrightarrow{k_p} P_{i+1jklm} \quad k > 0 \tag{6}$$
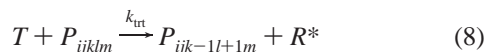
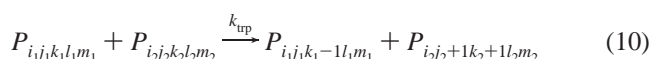$$P_{ijklm} + M \xrightarrow{k_p} P_{i+1jklm} \quad m > 0 \tag{7}$$

Equation 6 accounts for propagation by the addition of a monomer unit to an active radical while eq 7 accounts for propagation by monomer addition to an unrelaxed radical.

RAFT transfer

$$T + P_{ijklm} \xrightarrow{k_{trt}} P_{ijk-1l+1m} + R* \tag{8}$$

$$P_{i_1j_1k_1l_1m_1} + P_{i_2j_2k_2l_2m_2} \xrightarrow{k_{trt}} P_{i_1j_1k_1-1l_1+1m_1} + P_{i_2j_2k_2l_2-1m_2+1} \tag{9}$$

Equation 8 accounts for the initial reaction between the RAFT agent, T, and an active radical, $R*$, during the course of which a radical is released. Equation 9 accounts for RAFT transfer between two polymer chains, one with an active radical that becomes capped and the other with an inactive (capped) radical that becomes unrelaxed.

Intermolecular chain transfer

$$P_{i_1j_1k_1l_1m_1} + P_{i_2j_2k_2l_2m_2} \xrightarrow{k_{trp}} P_{i_1j_1k_1-1l_1m_1} + P_{i_2j_2+1k_2+1l_2m_2} \tag{10}$$

$$P_{i_1j_1k1l_1m_1} + P_{i_2j_2k_2l_2m_2} \xrightarrow{k_{trp}} P_{i_1j_1k_1l_1m_1-1} + P_{i_2j_2+1k_2l_2m_2+1} \tag{11}$$

Equations 10 and 11 account for chain transfer between two different polymer chains. In these reactions, the first polymer chain transfers an active or unrelaxed radical to the second chain resulting in the latter having a new site on the polymer backbone at which a branch can form.

Intramolecular chain transfer

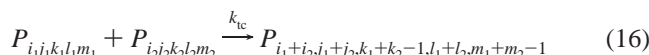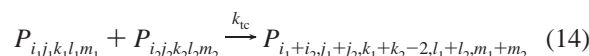$$P_{ijklm} \xrightarrow{k_{intr}} P_{ij+1klm} \tag{12}$$

Equation 12 accounts for the back-biting reaction in which short-chain branches are produced via a cyclic transition state in which the chain-end radical abstracts a hydrogen atom from a carbon atom that is a few (usually four) carbons back from the active chain end.

Relaxation

$$P_{ijklm} \xrightarrow{k_r} P_{ijk+1lm-1} \tag{13}$$

Equation 13 represents the relaxation reaction which has been proposed to account for the experimentally observed suppression of branching in RAFT. In this first-order decay reaction, the unrelaxed radical is transformed into an active radical which can then participate in intramolecular chain transfer to polymer.

Termination by combination

$$P_{i_1j_1k_1l_1m_1} + P_{i_2j_2k_2l_2m_2} \xrightarrow{k_{tc}} P_{i_1+i_2,j_1+j_2,k_1+k_2-2,l_1+l_2,m_1+m_2} \tag{14}$$

$$P_{i_1j_1k_1l_1m_1} + P_{i_2j_2k_2l_2m_2} \xrightarrow{k_{tc}} P_{i_1+i_2,j_1+j_2,k_1+k_2,l_1+l_2,m_1+m_2-2} \tag{15}$$

$$P_{i_1j_1k_1l_1m_1} + P_{i_2j_2k_2l_2m_2} \xrightarrow{k_{tc}} P_{i_1+i_2,j_1+j_2,k_1+k_2-1,l_1+l_2,m_1+m_2-1} \tag{16}$$

Equation 14 accounts for bimolecular termination by combination between two active radicals. Similarly, eqs 15 and 16 account for termination between two unrelaxed radicals and an active and unrelaxed radical, respectively.

2.4. Assumptions. The following assumptions were made in deriving the mathematical model for the kinetics scheme discussed above.

(1) In the propagation reaction eq 6, the rate of the reaction is proportional to (a) the concentration of monomer and (b) the number of active (uncapped) radicals in the polymer chain. Similarly, in the propagation reaction eq 7, the rate of the reaction is proportional to (a) the concentration of monomer and (b) the number of unrelaxed (just uncapped) radicals in the polymer chain.

(2) The propagation reactions eqs 6 and 7 have the same rate constant, k_p.

(3) The rate of propagation from a tertiary radical produced by either intermolecular and intramolecular chain transfer is much lower than that from a "normal" chain-end radical. However, the rate constant for propagation from all radicals has been assumed to be the same in order to maintain simplicity.

(4) In the RAFT transfer reaction eq 8, the rate of the reaction is proportional to (a) the concentration of the RAFT agent and (b) the number of active (uncapped) radicals in the polymer chain to which the RAFT agent is being transferred.

(5) In the RAFT transfer reaction eq 9, the rate of the reaction is proportional to (a) the number of active (uncapped) radicals in the polymer chain to which the RAFT agent is being transferred and (b) the number of inactive (capped) radicals in the polymer chain from which the RAFT agent is being transferred.

(6) In the intermolecular chain transfer to polymer reaction eq 10, the rate of the reaction is proportional to (a) the number of repeat units in the polymer receiving the chain and (b) the number of active (uncapped) radicals in the polymer from which the chain is being transferred. Similarly, in the intermolecular chain transfer to polymer reaction eq 11, the rate of the reaction is proportional to (a) the number of repeat units in the polymer receiving the chain and (b) the number of unrelaxed (just uncapped) radicals in the polymer from which the chain is being transferred.

(7) The intermolecular chain transfer to polymer reactions eqs 10 and 11 have the same rate constant, k_{trp}.

(8) In the intramolecular chain transfer to polymer reaction eq 12, the rate of the reaction is proportional to the number of active (uncapped) radicals in the polymer chain.

(9) In the relaxation reaction eq 13, the rate of the reaction is proportional to the number of unrelaxed (just uncapped) radicals in the polymer chain undergoing relaxation.

(10) In the termination by combination reaction eq 14, the rate of the reaction is proportional to the number of active (uncapped) radicals in the polymer chains participating in the reaction. Similarly, in the termination by combination reaction eq 15, the rate of the reaction is proportional to the number of unrelaxed (just uncapped) radicals in the polymer chains participating in the reaction.

(11) In the termination by combination reaction eq 16, the rate of the reaction is proportional to (a) the number of active (uncapped) radicals in the first polymer chain and (b) the number of unrelaxed (just uncapped) radicals in the second polymer chain participating in the reaction.

(12) The termination by combination reactions eqs 14−16 have the same rate constant, k_{tc}.

2.5. Mass Balances. The general mass balance for a polymer chain P_{ijklm} is given below.

$$\frac{dP_{ijklm}}{dt} = k_p C_M k(-P_{ijklm} + P_{i-1jklm})$$

$$+ k_p C_M m(-P_{ijklm} + P_{i-1jklm})$$

$$+ k_{trt} C_{RAFT}(-kP_{ijklm} + (k+1)P_{ijk+1l-1m})$$

$$- k_{trt} k P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} l_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$- k_{trt} l P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} k_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{trt}(k+1) P_{ijk+1l-1m} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} l_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{trt}(l+1) P_{ijkl+1m-1} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} k_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$- k_{trp} k P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} i_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$- k_{trp} i P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} k_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{trp}(k+1) P_{ijk+1lm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} i_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{trp} i P_{ij-1k-1lm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} k_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$- k_{trp} m P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} i_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$- k_{trp} i P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} m_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{trp}(m+1) P_{ijklm+1} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} i_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{trp} i P_{ij-1klm-1} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} m_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ k_{intr} k(-P_{ijklm} + P_{ij-1klm})$$

$$+ k_r[-mP_{ijklm} + (m+1)P_{ijk-1lm+1}]$$

$$- k_{tc} k P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} k_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ \frac{1}{2} k_{tc} \sum_{i_1=1}^{i}\sum_{j_1=0}^{j}\sum_{k_1=0}^{k+2}\sum_{l_1=0}^{l}\sum_{m_1=0}^{m} [k_1 P_{i_1 j_1 k_1 l_1 m_1}$$
$$(k+2-k_1)P_{i-i_1,j-j_1,k+2-k_1,l-l_1,m-m_1}]$$

$$- k_{tc} m P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} m_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ \frac{1}{2} k_{tc} \sum_{i_1=1}^{i}\sum_{j_1=0}^{j}\sum_{k_1=0}^{k}\sum_{l_1=0}^{l}\sum_{m_1=0}^{m+2} [m_1 P_{i_1 j_1 k_1 l_1 m_1}(m+2-m_1)$$
$$P_{i-i_1,j-j_1,k-k_1,l-l_1,m+2-m_1}]$$

$$- k_{tc} k P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} m_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$- k_{tc} m P_{ijklm} \sum_{i_1=1}^{\infty}\sum_{j_1=0}^{\infty}\sum_{k_1=0}^{\infty}\sum_{l_1=0}^{\infty}\sum_{m_1=0}^{\infty} k_1 P_{i_1 j_1 k_1 l_1 m_1}$$

$$+ \frac{1}{2} k_{tc} \sum_{i_1=1}^{i}\sum_{j_1=0}^{j}\sum_{k_1=0}^{k+1}\sum_{l_1=0}^{l}\sum_{m_1=0}^{m+1} [k_1 P_{i_1 j_1 k_1 l_1 m_1}(m+1-m_1)$$
$$P_{i-i_1,j-j_1,k+1-k_1,l-l_1,m+1-m_1}]$$

$$+ \frac{1}{2} k_{tc} \sum_{i_1=1}^{i}\sum_{j_1=0}^{j}\sum_{k_1=0}^{k+1}\sum_{l_1=0}^{l}\sum_{m_1=0}^{m+1} [m_1 P_{i_1 j_1 k_1 l_1 m_1}(k+1-k_1)$$
$$P_{i-i_1,j-j_1,k+1-k_1,l-l_1,m+1-m_1}] \quad (17)$$

Here, C_M and C_{RAFT} represent the concentrations of monomer and RAFT agent, respectively.

In this mass balance, the term, $k_p C_M k(-P_{ijklm} + P_{i-1jklm})$ accounts for loss and formation of the polymer chain by propagation at an active radical (eq 6). Similarly, the term $k_p C_M m(-P_{ijklm} + P_{i-1jklm})$ accounts for propagation at an unrelaxed radical (eq 7). The term $k_{trt} C_{RAFT}(-kP_{ijklm} + (k+1)P_{ijk+1l-1m})$ accounts for the initial capping of active radicals by a RAFT agent molecule (eq 8). The next two terms account for loss of polymer chain P_{ijklm} by RAFT transfer (eq 9). In this reaction, polymer chain P_{ijklm} can be consumed in two ways. The first of these two terms accounts for loss of the polymer chain by the capping of one of its active radicals while the second term accounts for loss of the polymer chain by the uncapping of one of its capped radicals. The remaining terms are similarly obtained from the reaction scheme discussed above. It should be noted that the mass balance for the polymer chain P_{10100} also includes the term $k_i C_M C_R$ from eq 5, where C_R represents the concentration of free radicals in the system.

The method of moments[56] was then used to derive the population balance equations from the general polymer chain balance, eq 17 (the complete derivations have been provided as Supporting Information). These mass balances, listed in Appendix B, form a closed set of equations, and therefore, the use of closure approximations was unnecessary. Further, in the absence of a RAFT agent, the model formulated reduces to a model of conventional free-radical polymerization.

2.6. Prediction of Important Properties. The following property predictions can be obtained from the moments de-

scribed above. These measurements will be used in discussing the effects of RAFT transfer and relaxation on average polymer properties. All properties are cumulative.

(A) Conversion. In this study, only batch polymerizations of vinyl acetate are studied. Therefore, conversion can be calculated by the relatively simple expression below:

$$\text{Conversion} = \frac{\mu_{10000}}{\mu_{10000} + C_M} \quad (18)$$

Here, μ_{10000} is the concentration of repeat units in the polymer chains.

(B) Number Average Molecular Weight.

$$M_n = \text{MW}_{VA} \frac{\mu_{10000}}{\mu_{00000}} \quad (19)$$

Here, MW_{VA} is the molecular weight of vinyl acetate and μ_{00000} is the zeroth moment (i.e., the concentration of polymer chains in the system).

(C) Weight Average Molecular Weight.

$$M_w = \text{MW}_{VA} \frac{\mu_{20000}}{\mu_{10000}} \quad (20)$$

Here, μ_{20000} is the second moment with respect to the number of repeat units.

(D) Polydispersity.

$$\text{Pd} = \frac{M_w}{M_n} \quad (21)$$

(E) Branching Frequency. Branching frequency is defined as the number of branches per 1000 repeat units:

$$\text{branching frequency} = \frac{1000\mu_{01000}}{\mu_{10000}} \quad (22)$$

Here, μ_{01000} is the first moment with respect to the number of branches (i.e., the concentration of branches in the polymer chain).

(F) Average Number of Branches per Polymer Chain.

average number of branches per

$$\text{polymer chain} = \frac{\mu_{01000}}{\mu_{00000}} \quad (23)$$

(G) Average Segment Length. A segment is defined as a part of the polymer chain with either a radical (active, inactive, unrelaxed, or terminated) or a branch at each end. The total number of segments in the system is equal to the total number of polymer chains in the system plus twice the total number of branches in the system. This is because a linear polymer chain is defined as having a single segment. Further, the addition of each new branch point results in the creation of two new segments. For example, it can be verified that a polymer chain with a single branch has three segments while a polymer chain with two branches has five segments.

$$\text{average segment length} = \frac{\mu_{10000}}{\mu_{00000} + 2\mu_{01000}} \quad (24)$$

(H) Average Segment Length/NACL. Here, NACL denotes the number average chain length ($= \mu_{10000}/\mu_{00000}$). The metric "average segment length/NACL" indicates the level of branching

in the system. When there is no branching in the system (i.e., all polymer chains are linear), the value of this metric is equal to one. On the other hand if all the polymer chains each have a single branch, then this metric takes a value of $1/3$.

average segment length/NACL =

$$\frac{\mu_{10000}}{\mu_{00000} + 2\mu_{01000}}\left(\frac{\mu_{00000}}{\mu_{10000}}\right) \quad (25)$$

2.7. Parameter Estimation. Parameter estimation for the model formulated above was undertaken in gPROMS (Process Systems Enterprise, UK) using conventional bulk polymerization data for vinyl acetate found in the literature.[59] Of the eight kinetics model parameters, the intramolecular chain transfer to polymer constant k_{intr} was not estimated as it has no effect on the three measurements available. There is much discussion in the literature on the absolute values of RAFT transfer rate constants.[19,20] Further, it has been observed that accurate estimation of these parameters necessitates the availability of data pertaining to radical concentrations.[20] Therefore, though data for the RAFT bulk polymerization of vinyl acetate is available in the literature,[66,67] the RAFT transfer constant k_{trt} and the relaxation constant k_r were not estimated. In the rest of this study, they are treated as free parameters and analyses are conducted by systematically varying them. Only the numerical values of these rate constants are given in the text of the following sections; the units of these rate constants are consistent with those given in Table 1. Finally, a correlation for vinyl acetate from the literature[60] was used to account for the gel effect:

$$k_{tc} = k_{tc,0} \exp(-At) \quad (26)$$

where the time t is in seconds and

$$A = 5.81 \times 10^{-3} C_{I,0}^{0.2} \quad (27)$$

Here $C_{I,0}$ is the initial concentration of the initiator.

Figure 1 shows a comparison of the model predictions and the experimental data used for parameter estimation.[59] As can be seen, the fit for polydispersity is not as good as for the other two measurements, conversion and number average molecular weight. The inaccuracies in the prediction for conversion were attributed to the fact that a simple kinetics scheme was adopted and important effects such as initiator efficiency and chain transfer to monomer were neglected.

Table 1 lists the estimated model parameters and values found in the literature. As can be seen, though the model predictions do not fit perfectly with the data, the estimated values are similar to those found in the literature indicating that any inaccuracies in the predictions can be attributed to unmodelled phenomena.

3. Effects of RAFT on Intermolecular Chain Transfer to Polymer as Predicted by the Proposed RAFT Kinetics Scheme

In this section, the effects of RAFT on intermolecular chain transfer to polymer are studied. In order to determine the effects of RAFT transfer (eqs 8 and 9) on the properties identified above, four sets of simulations were undertaken. The first simulation corresponded to the experimental data used for parameter estimation[59] and represents the conventional bulk polymerization of vinyl acetate. In the remaining three simulations, the value of k_r, the rate constant of the relaxation reaction eq 13, was set at 10^6 s^{-1} so that this reaction did not influence
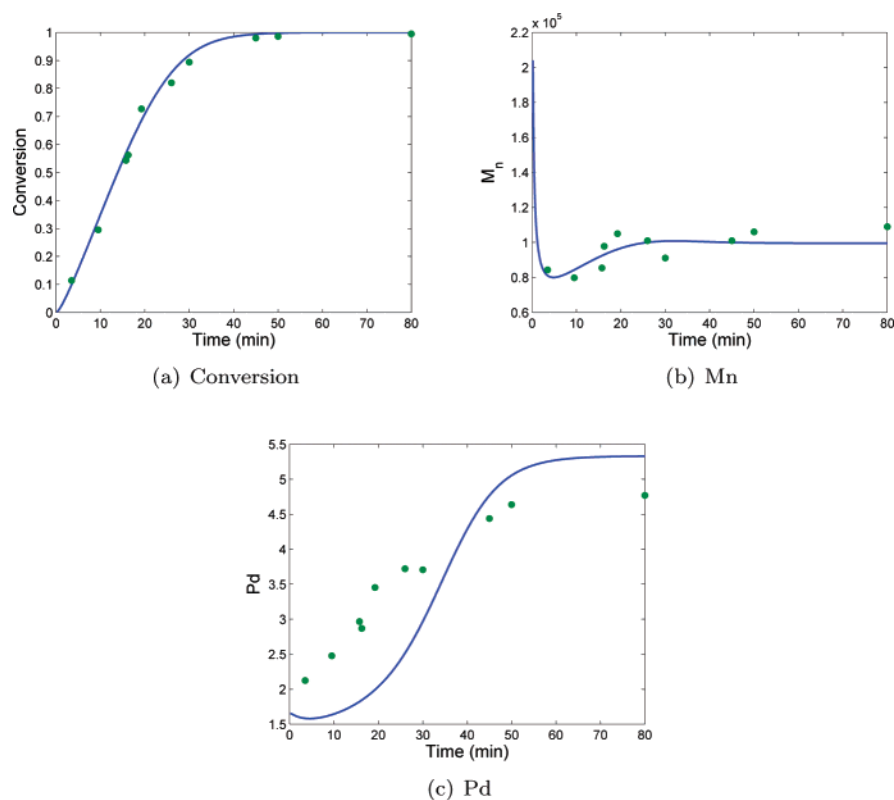
(a) Conversion

(b) Mn

(c) Pd

Figure 1. Comparison of the model predictions with the data used for parameter estimation.

Table 1. Estimated Model Parameters

Parameter	Unit	Value	Literature Values	Reference
k_d	s^{-1}	5.5067×10^{-4}	2.8523×10^{-5}	Hace et al. [57]
			1.74×10^{-4}	Znoj et al. [58]
			2.8508×10^{-4}	Baade et al., [59] Taylor & Reichert [60]
k_i	L mol^{-1} s^{-1}	12×10^{-4}	none found	
k_p	L mol^{-1} s^{-1}	2576.7	2367.2	Kalfas et al. [61]
			8182.1	Hutchison et al. [62]
			8321.1	Beuermann & Buback [63]
			9500	Baade et al., [59] Taylor & Reichert [60]
			11775	Hutchison et al. [64]
$k_{tc,0}$	L mol^{-1} s^{-1}	3.7717×10^8	2.9509×10^7	Kalfas et al. [61]
			3.55×10^8	Baade et al.,[59] Taylor & Reichert [60]
$C_{trp} = (k_{trp}/k_p)$	no units	2.5711×10^{-4}	2.36×10^{-4}	Tobita & Hatanaka [65]
			3.4×10^{-4}	Baade et al., [59] Kalfas et al. [61]
			5.2×10^{-4}	Taylor & Reichert [60]
k_{intr}	s^{-1}	0 (not estimated)		
k_{trt}	L mol^{-1} s^{-1}	0 (not estimated)		
k_r	s^{-1}	0 (not estimated)		

any measurements, while k_{trt}, the rate constant for the RAFT transfer reactions eqs 8 and 9, was taken to be 1000, 2500, and 5000 L mol^{-1} s^{-1}, respectively. In the literature, the rate of RAFT transfer for a particular RAFT agent and monomer is often reported as the ratio of the RAFT transfer rate constant to the propagation rate constant, $C_{tr} = k_{trp}/k_p$. The values of the RAFT transfer constant, k_{trp}, used in the simulations presented here, when expressed as this ratio C_{tr}, are similar in magnitude to those reported in the literature for RAFT agents such as thiocarbonylthio compounds[68] and xanthates[69,70] and monomers such as methyl methacrylate[68] and styrene.[68−70] Intramolecular chain transfer was neglected by setting the value of the intramolecular chain transfer rate constant k_{intr} to 0. The values for the remaining rate constants were those listed in Table 1. The initial concentrations of monomer and initiator were taken to be 10.82 and 0.0167 mol L^{-1} and corresponded to the experimental data used for parameter estimation.[59] In all

simulations of RAFT polymerization, the initial concentration of RAFT agent was taken to be five times the initial concentration of the initiator. As can be seen from Figure 2, under these conditions, the rate of the relaxation reaction eq 13 ($= k_r\mu_{00001}$) was equal to the rate of intermolecular RAFT transfer reaction eq 9 ($= k_{trt}\mu_{00100}\mu_{00010}$) indicating that relaxation was fast and limited only by the rate of RAFT transfer. It should be noted that the rates of RAFT transfer and relaxation are so similar that the corresponding lines in Figure 2 are practically indistinguishable.

Figure 3a depicts the conversion profiles under the four simulation conditions described above. As can be seen, increasing the rate of RAFT transfer results in an initial decrease in the rate of conversion. This is reasonable as when the rate of RAFT transfer is increased, the number of radicals being capped with the RAFT agent increases. This results in a decrease in the number of active radicals which, in turn, reduces the rate
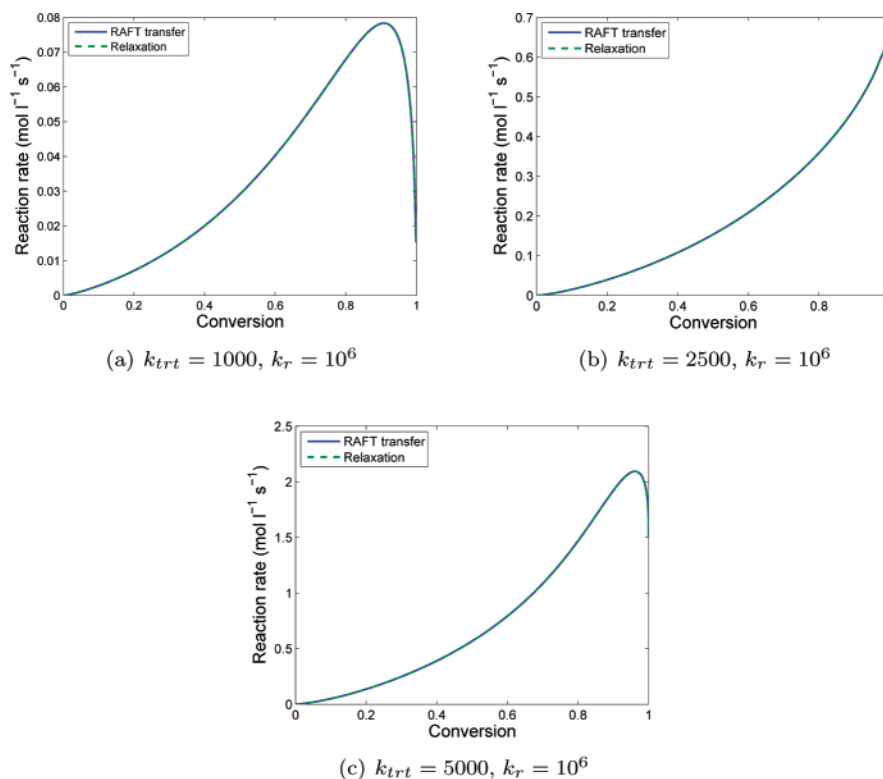
(a) $k_{trt} = 1000$, $k_r = 10^6$

(b) $k_{trt} = 2500$, $k_r = 10^6$

(c) $k_{trt} = 5000$, $k_r = 10^6$

Figure 2. Comparison of the rates of relaxation and RAFT transfer when relaxation is fast and the rate of RAFT transfer is progressively increased.

of conversion. However, as time progresses, the rate of conversion increases with an increase in the rate of RAFT transfer. This is because an increase in the rate of RAFT transfer results in an increase in the number of radicals in the system (from eq 8) resulting in the observed increase in conversion with further progression of the reaction.

From Figure 3b, it can be seen that as the RAFT transfer rate constant is increased, the number average molecular weight decreases indicating that increasing RAFT transfer results in shorter chains. This decrease in the length of the polymer chains is partly due to the extra radicals released by the initial RAFT transfer (eq 8). Further, increased capping of radicals decreases the number of active radicals which in turn decreases the rate of termination by disproportionation. Thus, these two features contribute to a net reduction in the number average molecular weight as the rate of RAFT transfer is increased. It should be noted that the decrease in number average molecular weight at high conversions is partly due to the experimental data[59] used for parameter estimation which indicated that as the reaction neared completion, a significant amount of initiator was still available. The resulting availability of radicals together with the small amount of monomer available results in the formation of a large number of short polymer chains at high conversions. This coupled with the inaccurate estimation of conversion mentioned above is the cause for the drop in number average molecular weight observable from Figure 3b.

From Figure 3c, it can be seen that as the rate of RAFT transfer is increased, there is a reduction in the weight average molecular weight. A typical feature of RAFT polymerization is that the polydispersity is relatively constant with conversion.[1] This is evident from Figure 3d which indicates that at the values of k_{trt} considered, the polydispersity remains relatively constant for most of the reaction. Further, at these values of k_{trt}, the polydispersity at full conversion is less than that for conventional bulk polymerization, which is again a typical feature of RAFT polymerization.[1]

Figure 3e indicates that, in the absence of the proposed relaxation mechanism, RAFT transfer has no effect on the rate of branching in the polymer chain as measured by the branching frequency. However, due to the reduction in the length of chains produced by an increase in the rate of RAFT transfer (as is evident from Figure 3b), the average number of branches per polymer chain, as shown in Figure 3f, decreases. Thus, it can be concluded that, in the absence of relaxation, the use of a RAFT agent essentially makes the chains shorter without affecting intermolecular chain transfer to polymer.

From Figure 3g, it can be seen that increasing the rate of RAFT transfer results in a decrease in the average length of segments in the polymer chains. This can be attributed to the fact that as the rate of RAFT transfer is increased, the number of chains in the system increases thus resulting in a greater number of segments. For example, if a polymer chain with one branch (and therefore three segments) is divided into two polymer chains, the number of segments increases to four. However, the increase in the number of segments is not as large as the increase in the number of chains and the overall effect is that as the rate of RAFT transfer is increased, the fraction of linear polymer chains in the system increases. This results in an increase in the ratio of the average segment length to the number average molecular weight seen in Figure 3h.

Thus, it can be concluded that as the rate of RAFT transfer is increased, in the absence of relaxation, more chains are created, with the average chain being shorter and less branched than in conventional polymerization.

4. Effects of RAFT on Intramolecular Chain Transfer to Polymer as Predicted by the Proposed RAFT Kinetics Scheme

As mentioned above, using data corresponding to conversion and polydispersity does not enable the estimation of the rate
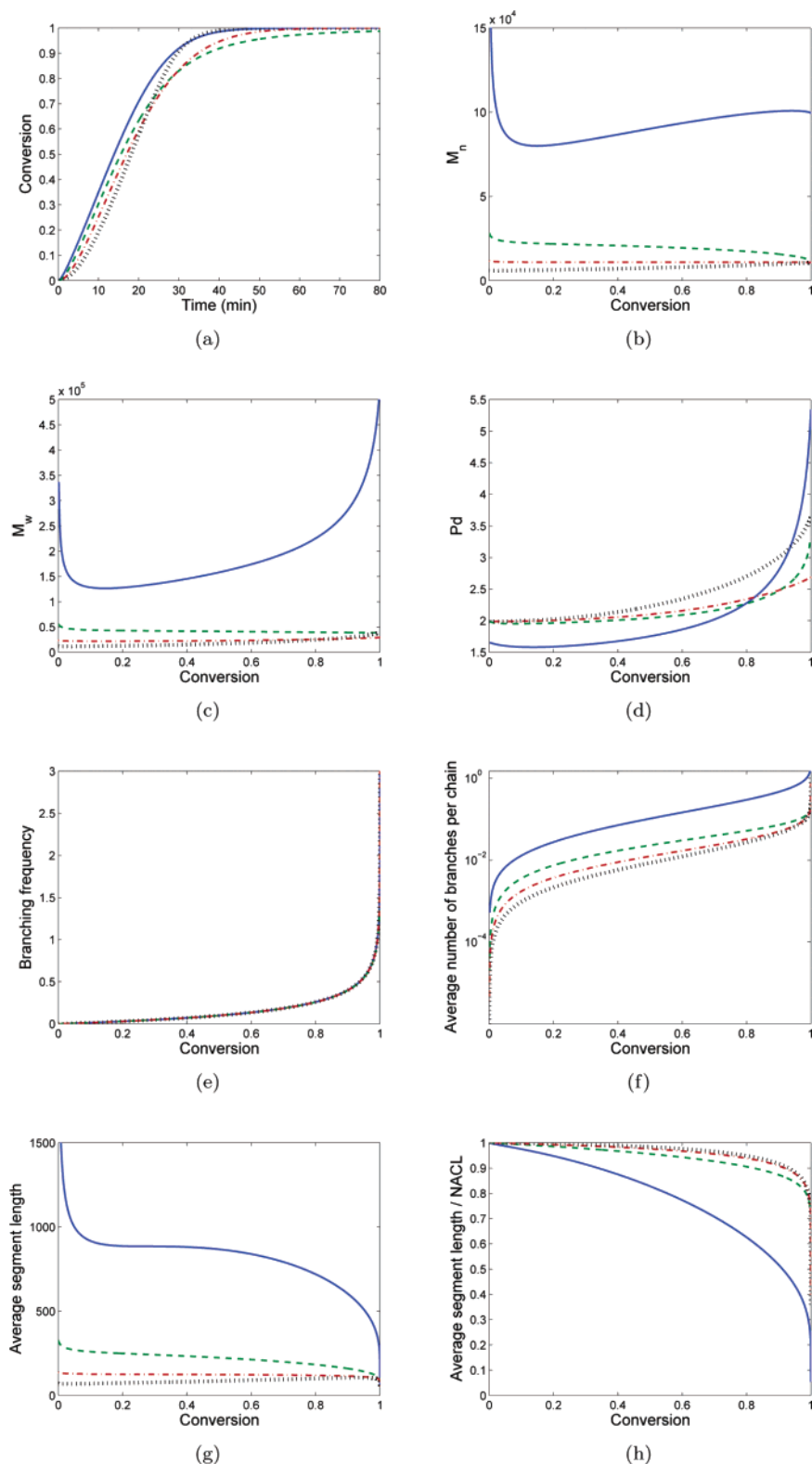
Figure 3. Variation of predicted properties with conversion: effect of increasing RAFT transfer when relaxation is fast. (—) Conventional bulk polymerization; (- - -) $k_{trt} = 1000$, $k_r = 10^6$; (- · - · -) $k_{trt} = 2500$, $k_r = 10^6$; (· · ·) $k_{trt} = 5000$, $k_r = 10^6$.

constant for intramolecular chain transfer to polymer. Therefore, four simulations were conducted in which the values of the rate constant for relaxation (eq 13) and intramolecular chain transfer to polymer (eq 12) were varied. In the first two simulations, the value of k_r was kept constant at 200 s^{-1} and the value of k_{intr}, the rate constant for intramolecular chain transfer, was increased from 100 to 200 s^{-1}. In the second pair of simulations, k_r was kept constant at 100 s^{-1} and k_{intr} was again increased

from 100 to 200 s^{-1}. The value of k_{trt}, the rate constant for RAFT transfer (eqs 8 and 9), was kept constant at 5000 L mol^{-1} s^{-1}. The values used for the remaining rate constants were those reported in Table 1. The initial conditions were the same as those described above. As can be seen from Figure 4, the values of k_r and k_{trt} used in these simulations correspond to the case where relaxation is slower than RAFT transfer and, hence, rate limiting.
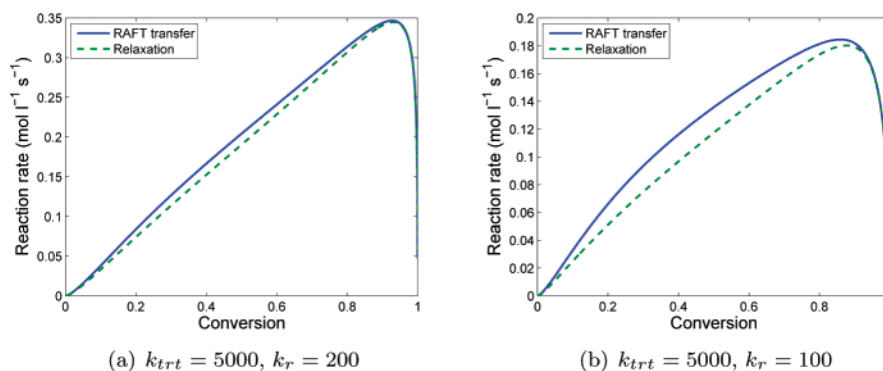
(a) $k_{trt} = 5000$, $k_r = 200$

(b) $k_{trt} = 5000$, $k_r = 100$

Figure 4. Comparison of the rates of relaxation and RAFT transfer when the relaxation is rate limiting.

(a) $k_{intr} = 100$, $k_r = 200$

(b) $k_{intr} = 200$, $k_r = 200$

(c) $k_{intr} = 100$, $k_r = 100$

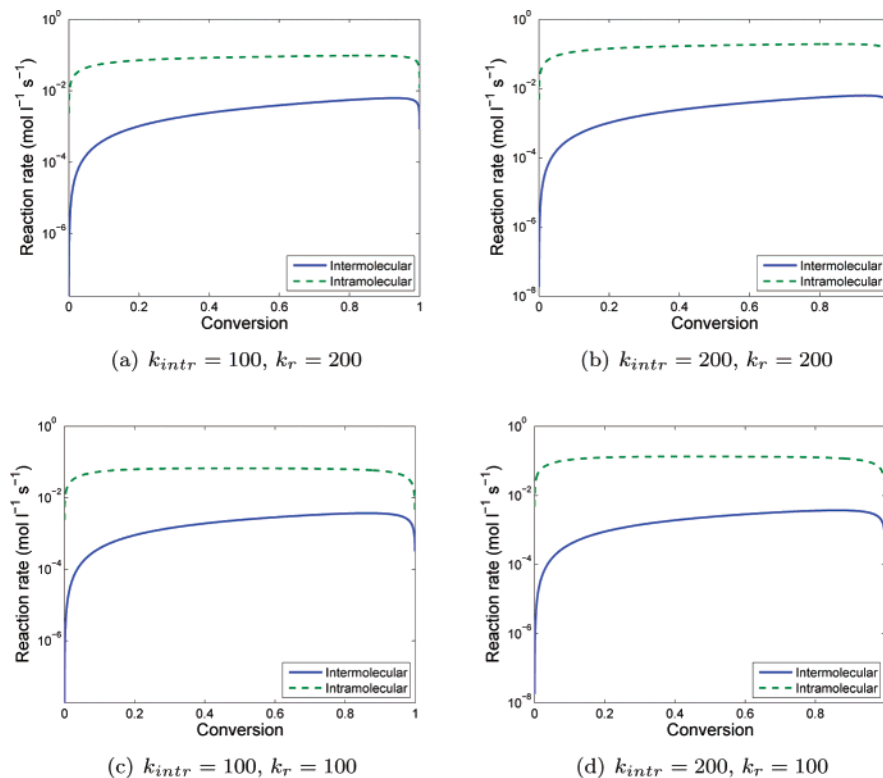(d) $k_{intr} = 200$, $k_r = 100$

Figure 5. Comparison of the rates of intermolecular and intramolecular chain transfer under increased relaxation times and increasing intramolecular chain transfer.

Figure 5 depicts the rates of intramolecular ($= k_{intr}\mu_{00100}$) and intermolecular ($= k_{trp}\mu_{00100}\mu_{10000}$) chain transfer to polymer under the conditions described above. It can be seen from Figure 5a and c (or Figure 5b and d) that as relaxation times are increased (i.e., as the value of k_r is reduced), the rate of intramolecular chain transfer to polymer is reduced while the rate of intermolecular chain transfer to polymer is unaffected. This is reasonable as increased relaxation times would result in unrelaxed radicals taking longer to become active and capable of intramolecular chain transfer to polymer. However, as both active and unrelaxed radicals can participate in intermolecular chain transfer to polymer, this reaction can be expected to be unaffected by increased relaxation times.

Figure 6 depicts the results obtained from the simulations described above. Figure 6a indicates that increasing the rate of intramolecular chain transfer to polymer does not have an effect on the rate of conversion. In view of assumption 3, this is reasonable as increasing intramolecular chain transfer to polymer only results in an increase in chain transfer without affecting the total number of radicals in the system. From Figure 6b, it can be seen that increasing the relaxation time (i.e., reducing

the value of k_r) results in a marginal increase in the number average molecular weight. The reason for this is that as the relaxation time is increased, unrelaxed radicals take longer to become active and capable of being capped by a RAFT radical. This phenomenon also results in the increase in the weight average molecular weight and polydispersity as seen in Figure 6c and d, respectively.

Figure 6e indicates that increasing the rate of intramolecular chain transfer to polymer increases the branching frequency. This is expected as increased chain transfer results in a higher probability of a new branch being formed in a given time period thus increasing the branching frequency in the system. This increase in branching frequency results in the increase in the average number of branches per chain observable from Figure 6f. Figure 6e also indicates that increasing the relaxation time results in a reduction in the branching frequency. This is because increased relaxation times result in a lower concentration of active radicals capable of intramolecular chain transfer to polymer thus reducing the rate of branching. This reduction in the rate of branching results in the reduction in the average number of branches per chain evident from Figure 6f.
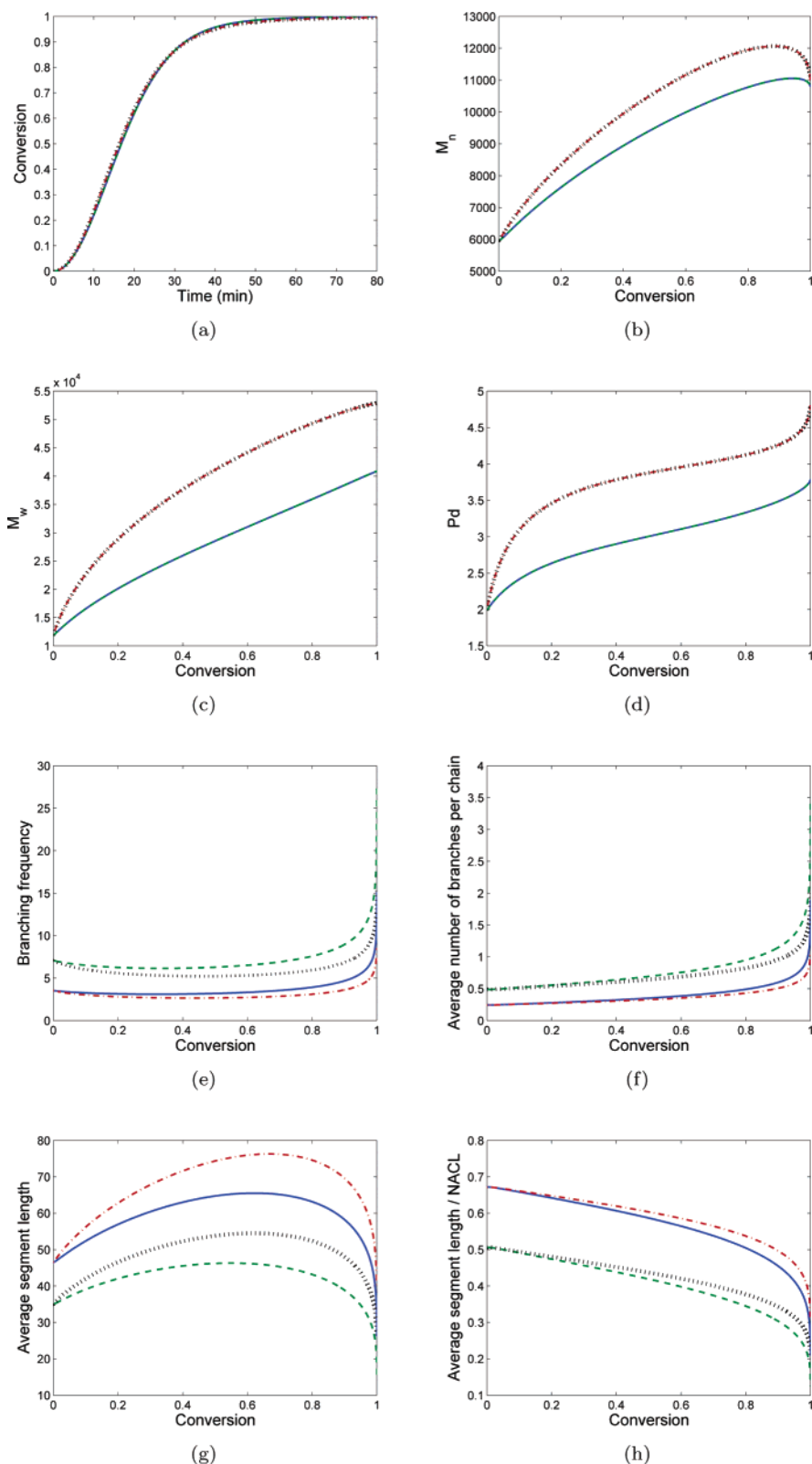
Figure 6. Variation of predicted properties with conversion: effect of having increasing intramolecular chain transfer and relaxation times. (—) $k_{intr} = 100$, $k_r = 200$; (- - -) $k_{intr} = 200$, $k_r = 200$; (- · - · -) $k_{intr} = 100$, $k_r = 100$; (· ·) $k_{intr} = 200$, $k_r = 100$.

Due to the increase in branching frequency when the rate of intramolecular chain transfer to polymer in increased, the average length of each segment is reduced as shown in Figure 6g. This in turn results in a reduction in the ratio of the average segment length to the number average chain length evident from Figure 6h. However, it is also evident from these two figures that increasing the relaxation time results in an increase in the average segment length and an increase in the linearity of the polymer chains. This increase is due to the fact that as relaxation times are increased, unrelaxed radicals propagate more before becoming active and capable of capping by RAFT transfer, thus increasing the length of each segment.

Thus, it can be concluded that increasing the relaxation times reduces the degree of branching in the system, essentially making the polymer chains more linear.

5. Conclusions

In this paper, a modified reaction scheme for RAFT transfer has been proposed. In this scheme, when a polymer chain loses a capped radical due to chain transfer, the radical first becomes "unrelaxed" before becoming active and capable of all reactions. In the unrelaxed state, it is proposed that these unrelaxed radicals are capable of undergoing propagation, intermolecular chain transfer to polymer, and bimolecular termination but not intramolecular chain transfer to polymer. Simulation-based analyses indicate that this assumption does not significantly or adversely effect the observed effects of RAFT on measurements such as conversion, number and weight average molecular weights, and polydispersity.

The assumption that unrelaxed radicals cannot undergo intramolecular chain transfer to polymer significantly affects other property predictions. As the lifetimes of these unrelaxed radicals are increased, that is, as the relaxation time is increased, the extent of branching in the system is reduced. This in turn results in polymer chains with fewer but longer branches. These polymer chains would therefore have a different hydrodynamic volume and intrinsic viscosity resulting in changes in the properties of the polymeric material being produced.

However, even in the absence of this assumption, i.e., even when relaxation is negligible, RAFT still appears to affect the rheology of the polymer formed. Although it does not appear to affect the rate of branching in the system, the typical characteristic of RAFT that it generates short polymer chains still results in the formation of more linear polymer chains. Essentially, increased RAFT transfer can be considered to result in the fragmentation into polymer chains smaller than those made by conventional means. In the presence of a RAFT agent, polymer chains would appear to be shorter and more linear with shorter branches, as observable from predictions of the average segment length and the ratio of the average segment length to the length of the polymer chains. Thus, a RAFT polymerization would generate chains with a different hydrodynamic volume and intrinsic viscosity than those prepared by conventional means.

Acknowledgment

Appendix A

Consider the kinetics scheme depicted in Table 2. This scheme is applicable to systems where a conventional chain transfer agent is used.

Here, termination by disproportionation is neglected. No attempt has been made to track doubly or triply branched live or dead chains, thus M_n^+, which represents two linear chains connected by a branch, is only singly subscripted. For simplicity, M_n^+ is assumed to not react further.

For conventional free-radical polymerization in the presence of chain transfer agent (CTA), a balance on live branched chains can be written as

$$\frac{dP^<}{dt} = k_{trp} P \sum_{n=1}^{\infty} n M_n - k_{tr} T P^< - k_{tc} P P^< - k_{tc}(P^<)^2 \quad (28)$$

Table 2. Kinetics Scheme for a System with a Conventional Chain Transfer Agent

radical decomposition	$I \xrightarrow{k_d} 2R$
initiation	$R + M \xrightarrow{k_i} P_1$
propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$
propagation from branch	$P_{n,m}^< + M \xrightarrow{k_p} P_{n,m+1}^<$
termination by combination	$P_n + P_m \xrightarrow{k_{tc}} M_{n+m}$
termination by combination	$P_n + P_{i,j}^< \xrightarrow{k_{tc}} M_{i,n+j}^<$
termination by combination	$P_{n,m}^< + P_{i,j}^< \xrightarrow{k_{tc}} M_{n+m+i+j}^+$
chain transfer to transfer agent	$P_n + T \xrightarrow{k_{trt}} M_n + T\cdot$
CTA initiation	$T\cdot + M \xrightarrow{k_{trp}} P_1$
chain transfer to polymer	$P_n + M_m \xrightarrow{k_{trp}} M_n + P_{m,0}^<$
chain transfer to branch polymer	$P_{n,m}^< + T \xrightarrow{k_{tr}} M_{n,m}^< + T\cdot$

Here, $P = \sum_{n=1}^{\infty} P_n$ and $P^< = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} P_{m,n}^<$.

Similarly, a balance on dead branched chains can be written as

$$\frac{dM^<}{dt} = k_{tc} P P^< + k_{tc}(P^<)^2 + k_{trt} T P^< \quad (29)$$

where $M^< = \sum_{n=1}^{\infty} M_n^<$.

Defining the total branched chains as $B^< = P^< + M^<$ and adding eqs 28 and 29 gives

$$\frac{dM^<}{dt} = k_{trp} P \sum_{n=1}^{\infty} n M_n \quad (30)$$

Thus, the total number of branched chains is independent of the chain transfer agent but the number of live branches is reduced by the chain transfer agent.

Likewise, a balance on the total number of repeat units in branched chains, $B^{tot} = \sum_{n=1}^{\infty} n B_n^< = \sum_{n=1}^{\infty}[nM_n^<] + \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} P_{m,n}^<$, can be written as

$$\frac{dB^{tot}}{dt} = k_p M P^< = k_p M \sum_{m=1}^{\infty}\sum_{n=1}^{\infty} P_{m,n}^< \quad (31)$$

Thus, a conventional chain transfer agent reduces the molecular weight of branched polmyers by reducing the number of live branches in the system.

Now, consider the kinetics scheme in Table 3 for RAFT polymerization.

Here, termination by combination has been neglected as it was seen above that it has no effect on the number of branched chains in the system.

Proceeding as before, a balance on live branched chains, $P^<$, can be written as

$$\frac{dP^<}{dt} = k_{trp} P \sum_{n=1}^{\infty} n M_n - k_{trt} P^< M + k_{trt} P M^< + k_{trp} P M^< \quad (32)$$

$$\Rightarrow \frac{dP^<}{dt} = k_{trp} P \sum_{n=1}^{\infty} n M_n + k_{trp} P M^< \quad (33)$$

Table 3. Kinetics Scheme for a System with a Reversible Chain Transfer Agent

radical decomposition	$I \xrightarrow{k_d} 2R$
initiation	$R + M \xrightarrow{k_i} P_1$
propagation	$P_n + M \xrightarrow{k_p} P_{n+1}$
propagation from branch	$P_{n,m}^< + M \xrightarrow{k_p} P_{n,m+1}^<$
chain transfer to polymer	$P_n + P_m \xrightarrow{k_{trp}} M_n + P_{m,0}^<$
chain transfer to polymer	$P_n + M_{i,j}^< \xrightarrow{k_{trp}} M_n + P_{i,+j}^+$
chain transfer to polymer	$P_{n,m}^< + M_{i,j}^< \xrightarrow{k_{trp}} M_{n,m}^< + P_{i+j}^+$
chain transfer to transfer agent	$P_n + TM_i + M_{i,j}^< \xrightleftharpoons{k_{trt}} TM_n + P_i$
chain transfer to transfer agent	$P_{n,m}^< + TM_i \xrightleftharpoons{k_{trt}} TM_{n,m}^< + P_1$
chain transfer to transfer agent	$P_{n,m}^< + TM_{i,j}^< \xrightleftharpoons{k_{trt}} TM_{n,m}^< + P_{i,j}^<$

Thus, employing the kinetics scheme depicted in Table 3, it appears that RAFT does not affect the number of live branched chains as does a conventional chain transfer agent.

Appendix B

The mass balances for the model formulated above are presented below. The derivations of the population balances are provided as Supporting Information.
Initiator

$$\frac{dC_I}{dt} = -k_d C_I \tag{34}$$

Here, C_I represents the concentration of initiator in the system.
Free radicals

$$\frac{dC_R}{dt} = 2k_d C_I - k_i C_M C_R + k_{trt} C_{RAFT} \mu_{00100} \tag{35}$$

Monomer

$$\frac{dC_M}{dt} = -k_i C_M C_R - k_p C_M \mu_{00100} - k_p C_M \mu_{00001} \tag{36}$$

RAFT agent

$$\frac{dC_{RAFT}}{dt} = -k_{trt} C_{RAFT} \mu_{00100} \tag{37}$$

Zeroth moment

$$\frac{d\mu_{00000}}{dt} = k_i C_M C_R - \frac{1}{2} k_{tc} (\mu_{00100})^2 - \frac{1}{2} k_{tc} (\mu_{00001})^2 - k_{to} \mu_{00100} \mu_{00001} \tag{38}$$

First moment with respect to (wrt) the number of repeat units

$$\frac{d\mu_{10000}}{dt} = k_i C_M C_R + k_p C_M \mu_{00100} + k_p C_M \mu_{00001} \tag{39}$$

First moment wrt the number of branches

$$\frac{d\mu_{01000}}{dt} = k_{trp} \mu_{10000} \mu_{00100} + k_{trp} \mu_{10000} \mu_{00001} + k_{intr} \mu_{00100} \tag{40}$$

First moment wrt the number of active (uncapped) radicals

$$\frac{d\mu_{00100}}{dt} = k_i C_M C_R - k_{trt} C_{RAFT} \mu_{00100} - k_{trt} \mu_{00100} \mu_{00010} + k_r \mu_{00001} - k_{tc} (\mu_{00100})^2 - k_{to} \mu_{00100} \mu_{00001} \tag{41}$$

First moment wrt the number of inactive (capped) radicals

$$\frac{d\mu_{000010}}{dt} = k_{trt} C_{RAFT} \mu_{00100} \tag{42}$$

First moment wrt the number of unrelaxed (just uncapped) radicals

$$\frac{d\mu_{00001}}{dt} = k_{trt} \mu_{00010} \mu_{00100} - k_r \mu_{00001} - k_{tc} (\mu_{00001})^2 - k_{to} \mu_{00100} \mu_{00001} \tag{43}$$

Second moment wrt the number of repeat units

$$\frac{d\mu_{20000}}{dt} = k_i C_M C_R + k_p C_M (2\mu_{10100} + \mu_{00100}) + k_p C_M (2\mu_{10001} + \mu_{00001}) + k_{tc} (\mu_{10100})^2 + k_{tc} (\mu_{10001})^2 + 2k_{to} \mu_{10100} \mu_{10001} \tag{44}$$

Second moment wrt the number of repeat units and active (uncapped) radicals

$$\frac{d\mu_{10100}}{dt} = k_i C_M C_R + k_p C_M \mu_{00200} + k_p C_M \mu_{00101} - k_{trt} C_{RAFT} \mu_{10100} - k_{trt} \mu_{10100} \mu_{00010} - k_{trp} \mu_{10100} \mu_{10000} + k_{trp} \mu_{20000} \mu_{00100} + k_r \mu_{10001} - k_{to} \mu_{10100} \mu_{00100} - \frac{1}{2} k_{to} \mu_{10100} \mu_{00001} - \frac{1}{2} k_{to} \mu_{00100} \mu_{10001} \tag{45}$$

Second moment wrt the number of active (uncapped) radicals

$$\frac{d\mu_{00200}}{dt} = k_i C_M C_R + k_{trt} C_{RAFT} (\mu_{00100} - 2\mu_{00200}) + k_{trt} \mu_{00010} (\mu_{00100} - 2\mu_{00200}) + k_{trp} \mu_{10000} (\mu_{00100} - 2\mu_{00200}) + k_{trp} \mu_{00100} (2\mu_{10100} + \mu_{10000}) + k_r (2\mu_{00101} + \mu_{00001}) + k_{tc} [(\mu_{00200})^2 - 4\mu_{00200} \mu_{00100} + 2(\mu_{00100})^2] + 2k_{to} \mu_{00200} (\mu_{00101} - \mu_{00001}) + k_{to} \mu_{00100} (\mu_{00001} - 2\mu_{00101}) \tag{46}$$

Second moment wrt the number of repeat units and unrelaxed (just uncapped) radicals

$$\frac{d\mu_{10001}}{dt} = k_p C_M \mu_{00101} + k_p C_M \mu_{00002} + k_{trt} \mu_{10010} \mu_{00100} - k_{trp} \mu_{10001} \mu_{10000} + k_{trp} \mu_{20000} \mu_{00001} - k_r \mu_{10001} - k_{to} \mu_{10001} \mu_{00001} - \frac{1}{2} k_{to} \mu_{10100} \mu_{00001} - \frac{1}{2} k_{to} \mu_{10001} \mu_{00100} \tag{47}$$

Second moment wrt the number of active (uncapped) radicals and unrelaxed (just uncapped) radicals

$$\frac{d\mu_{00101}}{dt} = -k_{trt}C_{RAFT}\mu_{00101} - k_{trt}\mu_{00101}\mu_{00010} +$$
$$k_{trt}\mu_{00110}\mu_{00100} - 2k_{trp}\mu_{00101}\mu_{10000} + k_{trp}\mu_{10001}\mu_{00100} +$$
$$k_{trp}\mu_{10100}\mu_{00001} + k_r(\mu_{00002} - \mu_{00101} - \mu_{00001}) +$$
$$k_{tc}\mu_{00100}\mu_{00001} - \frac{3}{2}k_{tc}\mu_{00101}(\mu_{00100} + \mu_{00001}) -$$
$$\frac{1}{2}k_{tc}\mu_{00200}\mu_{00001} - \frac{1}{2}k_{tc}\mu_{00002}\mu_{00100} \quad (48)$$

Second moment wrt the number of repeat units and inactive (capped) radicals

$$\frac{d\mu_{10010}}{dt} = k_p C_M \mu_{00110} + k_p C_M \mu_{00011} + k_{trt}C_{RAFT}\mu_{10100} +$$
$$k_{trt}\mu_{10100}\mu_{00010} - k_{trt}\mu_{10010}\mu_{00100} \quad (49)$$

Second moment wrt the number of unrelaxed (just uncapped) radicals

$$\frac{d\mu_{00002}}{dt} = k_{trt}\mu_{00100}(2\mu_{00011} + \mu_{00010}) + k_{trp}(\mu_{00001} -$$
$$2\mu_{00002})\mu_{10000} + k_{trp}(2\mu_{10001} + \mu_{10000})\mu_{00001} - k_r(2\mu_{00002} -$$
$$\mu_{00001}) + k_{tc}[(\mu_{00002})^2 - 4\mu_{00002}\mu_{00001} + 2(\mu_{00001})^2] +$$
$$2k_{tc}\mu_{00002}(\mu_{00101} - \mu_{00100}) + k_{tc}\mu_{00001}(\mu_{00100} - 2\mu_{00101}) \quad (50)$$

Second moment wrt the number of active (uncapped) radicals and inactive (capped) radicals

$$\frac{d\mu_{00110}}{dt} = k_{trt}(C_{RAFT} + \mu_{00010})(\mu_{00200} - \mu_{00110} - \mu_{00100}) -$$
$$k_{trt}\mu_{00100}\mu_{00110} - k_{trp}\mu_{00110}\mu_{10000} + k_{trp}\mu_{10010}\mu_{00100} +$$
$$k_r\mu_{00011} - k_{tc}\mu_{00110}\mu_{00100} - \frac{1}{2}\mu_{00110}\mu_{00001} -$$
$$\frac{1}{2}\mu_{00011}\mu_{00100} \quad (51)$$

Second moment wrt the number of inactive (uncapped) radicals and unrelaxed (just uncapped) radicals

$$\frac{d\mu_{00011}}{dt} = k_{trt}(C_{RAFT} + \mu_{00010})\mu_{00101} + k_{trt}\mu_{00100}(\mu_{00020} -$$
$$\mu_{00011} - \mu_{00001}) - k_{trp}\mu_{00011}\mu_{10000} + k_{trp}\mu_{10010}\mu_{00001} -$$
$$k_r\mu_{00011} - k_{tc}\mu_{00110}\mu_{00001} - \frac{1}{2}k_{tc}\mu_{00110}\mu_{00001} -$$
$$\frac{1}{2}k_{tc}\mu_{00011}\mu_{00100} \quad (52)$$

Second moment wrt the number of inactive (capped) radicals

$$\frac{d\mu_{00020}}{dt} = k_{trt}(C_{RAFT} + \mu_{00010})(2\mu_{00110} + \mu_{00100}) +$$
$$k_{trt}\mu_{00100}(\mu_{00010} - 2\mu_{00020}) + k_{tc}(\mu_{00110})^2 +$$
$$k_{tc}(\mu_{00011})^2 + 2k_{tc}\mu_{00110}\mu_{00011} \quad (53)$$

Supporting Information Available: RAFT kinetic mechanism, mass balances, and derivation of moment mass balances.

This material is available free of charge via the Internet at http://pubs.acs.org.

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