# Molecular Weight Distributions in Free-Radical Polymerizations. 1. Model Development and Implications for Data Interpretation

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ABSTRACT: Many properties (e.g., film formation) of a polymer depend on the full molecular weight distribution (MWD) as well as on the averages of this distribution. Moreover, the MWD contains the complete kinetic history of a polymerization system, and hence an experimental MWD can yield considerable mechanistic information. Complete equations are developed which enable the MWD to be calculated for a wide range of straight-chain free-radical polymerizations. These equations also give insight into the qualitative form of the MWD, thus providing a method for extracting kinetic and mechanistic information from experimental MWDs. Methods are also described which enable numerical solutions to be obtained for the resulting nonlinear integrodifferential equations. The scheme takes into account initiation, transfer, propagation, and termination, allowing all of these to be dependent upon the degrees of polymerization of the chains involved. The model is applicable to bulk and solution polymerizations and to compartmentalized systems (conventional and micro- and miniemulsion polymerizations); in the latter case, phase-transfer events (radical entry into and exit from latex particles, and the aqueous phase kinetics of the various radical species) are specifically included. The dependence of the termination rate coefficient upon the lengths of both participating chains is especially important in systems where termination is kinetically significant. Approximate analytical solutions are also developed for a number of cases of interest. These show that the instantaneous number MWD at high molecular weights is a single exponential—even when termination occurs to a significant extent—which is a direct consequence of the chain-length dependence of termination rate coefficients, i.e., most termination events involve at least one very short chain. When the concentration of radicals in the system is low, the "decay constant" of the exponential part of the MWD is given by the ratio of transfer to propagation rate coefficients. In addition, the cumulative MWD frequently has the same behavior as the instantaneous MWD. This has the important implication that considerable mechanistic information can be obtained from size exclusion chromatography data by plotting ln(number MWD) against molecular weight. Such plots can reveal, for example, the termination mechanism that controls the MWD, values of transfer constants, and nucleation mechanisms in emulsion polymerization. Illustrative calculations are carried out for a number of systems. These verify the conclusions from the approximate analytic solutions and show also that the MWD in bulk or solution polymerizations at low conversions and high initiator concentrations is sensitive to the mode of termination (combination or disproportionation).

## 1. Introduction

The molecular weight distribution (MWD) of a polymer is a record of the kinetic history of the reactions which occurred during its formation. Therefore, it is an important source of information about the kinetic processes that have taken place in polymerization systems. Providing that this information can be extracted from the MWD in a sensible and unambiguous manner, insight can be gained into the processes by which new chains are born, grow, and die. This process of extraction of information from free-radical polymerization systems is inherently difficult for two main reasons: first, that chain-forming, -growing and -stopping events, which control the MWD, normally occur continuously throughout the course of a polymerization, making it difficult to separate effects from different sources, and second, that the mechanism of termination between two radical species, and therefore the form of the MWD, can change during the course of a polymerization[1–4] due to changes in the relative amounts of monomer and polymer in the system.

Averages of the molecular weight of a polymer are important because they affect many of the physical properties of the polymer. The literature[5] contains many correlations between mechanical properties and the average molecular weight of polymers. However, often the average molecular weight is not sufficient to describe the influence of molecular weights on many mechanical properties. One example[6] is the rate of film formation and the minimum film-forming temperature for a latex formed by emulsion polymerization. A simple average of the molecular weight distribution is not adequate for the purpose of properly characterizing this process.

Many methods for calculating the MWD in free-radical polymerization systems exist in the literature.[7–16] None, however, have properly taken account of the fact that termination rate coefficients are dependent upon the size (or length) of the radicals involved (an idea which was first suggested by Benson and North[17]) while at the same time providing understanding of the shape of the MWD. This therefore stands as the central aim of this work, to take proper account of the chain-length dependence of termination rate coefficients while retaining some connection between the physical and chemical processes occurring in the polymerization and the form of the MWD produced. The most complete and physically realistic model for termination developed so far is that of Russell et al.,[18,19] and therefore this work takes that model as its starting point. This work develops a quantitative description of the MWD which requires no simplifying assumptions as to the variation of the termination rate coefficient with chain length.

The overall objectives of this work are 2-fold: to provide a methodology for extracting kinetic information from both homo- and heterogeneous free-radical polym-

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erization systems in which chain formation is a continuous process and to predict the molecular weight distribution for systems in which the kinetics are well understood. Furthermore, if the MWD predicted in systems where the kinetics are thought to be well understood is different from that measured experimentally, then the applicability of the kinetic scheme in use must be questioned.

We start by examining a simple zero−one compartmentalized system, i.e., one in which the maximum number of radicals per locus of polymerization is one, which corresponds to Smith−Ewart cases 1 and 2.[20] We derive an exact analytical form for the MWD in this system that is equivalent to, but conceptually simpler than, previous work[9,13] for this system. We next give the equations governing the MWD in a zero−one−two system, including chain-length-dependent termination, and show that no simple analytical expression for the MWD exists. While numerical solutions of the MWD in this system can be obtained in principle, this was not implemented in the present work. These equations for the zero−one−two system are given here to provide a starting point for, and to establish a minimum level of theory that should be included in, future work. The major contribution of the present work is the third case, where we examine polymerization in the bulk or in systems in which compartmentalization is unimportant, so called pseudobulk systems, also equivalent to Smith−Ewart case 3.[20] For this case we derive an approximate analytical solution that allows the functional form, but not exact numerical values, of the MWD to be understood in terms of the rates of initiation, propagation, transfer, and chain-length-dependent termination. It is from this result that a large amount of understanding of the factors controlling the MWD can be gained. We then develop a method for numerical solution of the (pseudo)bulk MWD. Finally, we present illustrative calculations of the MWD in bulk or pseudobulk polymerizations under a variety of experimental conditions.

This work introduces a number of fundamental new results and has important implications for the interpretation of MWDs. The formalism of the derivation of the MWD used here leads to a novel method for plotting experimental MWDs, as the natural logarithm of the number of chains as a function of their length (or molecular weight), that allows the extraction of both qualitative and quantitative information. The most immediately applicable of these is that transfer constants or rate coefficients can be extracted from the high molecular weight portion of the MWD when plotted in this way. Of further interest is that the type of termination that occurs in a polymerization system (combination versus disproportionation) has a qualitative effect on the MWD when plotted in the manner suggested by this work, in the former case giving a curve with a maximum and in the latter a monotonically decreasing curve.

## 2. Zero−One Systems

The equations presented in this section are applicable to free-radical polymerization systems in which compartmentalization of radicals is important and specifically when the maximum number of radicals per locus of polymerization is one. Such systems can include emulsion, microemulsion, and miniemulsion polymerizations, although the equations presented here have been written using the notation and mechanistic information applicable to emulsion polymerizations.

### A. Equations Describing Radical Chain-Length Distribution and Molecular Weight Distribution.

The molecular weight distribution of a polymer is the distribution of molecular weights of dead polymer. For our purposes we will more often refer to the chain-length distribution (CLD), where "chain length" is equivalent to the number of monomer units contained in the chain. The MWD and CLD are trivially related by the molecular weight of the monomer unit. The CLD is found from the chain-length distribution of radicals (RCLD) and the rate of chain-stopping events. Therefore, before the MWD can be found the RCLD must be known.

The original approach of Smith and Ewart[20] for modeling the kinetics in this type of system was to write rate equations in terms of the fraction of latex particles with zero and one radical per particle. For the purpose of this work, which has the elucidation of molecular weight distributions as its aim, it is also necessary to take account of the length of the radicals in those particles which contain a radical. We define the fraction of particles with zero radicals as $R_0$ and the fraction of particles containing one radical with degree of polymerization $i$ as $R_{1,i}$.

In zero−one systems the following events can occur

(i) entry of initiator-derived radicals into particles, with first-order rate coefficient $\varrho_I$,

(ii) re-entry of radicals which have previously desorbed from a latex particle, with rate coefficient $\varrho_{re}$,

(iii) entry of radicals created by thermal processes either in the aqueous phase or on the surface of the latex particles, with rate coefficient $\varrho_{th}$,

(iv) desorption of monomeric radicals created by transfer, from latex particles into the aqueous phase, with rate coefficient $k_{dM}$,

(v) propagation of radicals within the particles, with rate coefficient $k_p^i$ for the $i$th propagation step or $k_p$ when chains are long, and

(vi) transfer of radical activity to monomer, with rate coefficient $k_{tr}$, which can then desorb or propagate.

By the definition of a zero−one system, entry of any species into a particle which already contains a radical is assumed to result in instantaneous termination, thereby ensuring that no particle can contain more than one radical. It is important to realize that in a zero−one system those species which enter as a result of initiator decomposition will have a length $z$[21] because in general initiator fragments are hydrophilic and only become surface-active after the addition of a few ($z$) monomer units, whereas those that re-enter from the continuous phase are monomeric in length ($i = 1$). For the purpose of simplicity, and due to a lack of definite information, radicals created by thermal processes will also be assumed to have a length $z$, thereby ensuring that they cannot immediately desorb. The total rate of entry, $\varrho$, is given by:

$$\varrho = \varrho_I + \varrho_{re} + \varrho_{th} \tag{1}$$

The model employed here for zero−one kinetics is based upon the work of Ugelstad and Hansen,[22] Nomura,[23] Asua et al.,[24,25] and Casey et al.[26,27] which takes into account the above events, particularly the realization that only monomeric radicals created by transfer can desorb and that taking account of the fate of desorbed free radicals is more complicated than previously assumed. This model is trivially extended to take into account the length of radicals in the $R_1$ particles. Here we allow $k_p$ to depend upon chain length for all degrees of polymerization, while realizing that realistically $k_p$ will only vary from the long-chain value over the first few propagation steps. We therefore have the following population balance equations:

$$\frac{\mathrm{d}R_{1,1}}{\mathrm{d}t} = \varrho_{\mathrm{re}}R_0 - \varrho R_{1,1} - k_{\mathrm{dM}}R_{1,1} + k_{\mathrm{tr}}[\mathrm{M}]\sum_{i=1}^{\infty}R_{1,i} - k_{\mathrm{tr}}[\mathrm{M}]R_{1,1} - k_{\mathrm{p}}^{1}[\mathrm{M}]R_{1,1} \quad (2)$$

$$\frac{\mathrm{d}R_{1,i}}{\mathrm{d}t} = \varrho_{\mathrm{A}}R_0\delta_{i,z} - \varrho R_{1,i} - k_{\mathrm{tr}}[\mathrm{M}]R_{1,i} + k_{\mathrm{p}}^{i-1}[\mathrm{M}]R_{1,i-1} - k_{\mathrm{p}}^{i}[\mathrm{M}]R_{1,i},\ i > 1 \quad (3)$$

where $\varrho_{\mathrm{A}} = \varrho_{\mathrm{I}} + \varrho_{\mathrm{th}}$ and $\delta_{i,z}$ is the Kronecker $\delta$ ($\delta_{i,j} = 1$, $i = j$; $\delta_{i,j} = 0$, $i \neq j$).

The value of $R_{1,i}$ can be found by making the steady-state approximation in equations 2 and 3:

$$R_{1,1} = \frac{\varrho_{\mathrm{re}}R_0 + k_{\mathrm{tr}}[\mathrm{M}]\bar{n}}{\varrho + k_{\mathrm{dM}} + k_{\mathrm{p}}^{1}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}]} \quad (4)$$

$$R_{1,i} = \frac{\varrho_{\mathrm{A}}R_0\delta_{i,z} + k_{\mathrm{p}}^{i-1}[\mathrm{M}]R_{1,i-1}}{\varrho + k_{\mathrm{tr}}[\mathrm{M}] + k_{\mathrm{p}}^{i}[\mathrm{M}]} \quad (5)$$

where the average number of radicals per particle, $\bar{n}$, is given by

$$\bar{n} = \sum_{i=1}^{\infty}R_{1,i} \quad (6)$$

and[26]

$$\varrho_{\mathrm{re}} = \frac{k_{\mathrm{tr}}[\mathrm{M}]\bar{n}}{\left(1 + \dfrac{k_{\mathrm{p}}^{1}[\mathrm{M}]}{k_{\mathrm{dM}}}\right)\left(1 + \dfrac{k_{\mathrm{t}}^{\mathrm{aq}}[\mathrm{T}^{\bullet}]}{k_{\mathrm{re}}N_{\mathrm{c}}/N_{\mathrm{A}}}\right) - (1 - \bar{n})} \quad (7)$$

$$[\mathrm{T}^{\bullet}] \approx (k_{\mathrm{d}}[\mathrm{I}]/k_{\mathrm{t}}^{\mathrm{aq}})^{1/2} \quad (8)$$

in which $k_{\mathrm{t}}^{\mathrm{aq}}$ is the termination rate coefficient for aqueous phase radicals ($\mathrm{T}^{\bullet}$), $N_{\mathrm{c}}$ is the number concentration of latex particles, and $k_{\mathrm{d}}$ is the rate coefficient for decomposition of initiator (I). The rate coefficient for re-entry of aqueous phase monomeric radicals into latex particles, $k_{\mathrm{re}}$, can be found[26] (at least in the absence of polymeric stabilizers) from the Smoluchowski equation with the further realization that the monomeric radical species will diffuse much more quickly than the latex particles and that the size of the latex particles is much larger than that of a monomeric radical. Hence

$$k_{\mathrm{re}} = 4\pi N_{\mathrm{A}}D_{\mathrm{mon}}^{\mathrm{aq}}r_{\mathrm{s}} \quad (9)$$

where $D_{\mathrm{mon}}^{\mathrm{aq}}$ is the diffusion coefficient of monomer in the aqueous phase and $r_{\mathrm{s}}$ is the swollen radius of the latex particle.

Equations 4–9 above define the RCLD for a zero–one system within the model of Casey et al.[26] Solution of these equations requires an iterative procedure in which $\bar{n}$ is guessed and then eqs 4, 5, and 7 are evaluated, after which a new value of $\bar{n}$ can be obtained from eq 6. The procedure is then repeated until convergence in $\bar{n}$ is achieved.

In this work we are especially concerned with the general form of the MWD, and this can be determined without numerically solving eqs 4–9. In this system there are two events which can lead to dead polymer: tranfer and entry. Transfer results in a dead chain with the same length as the radical which was involved in the transfer reaction, but re-entry will result in a dead chain with one more monomer unit and entry of initiator-derived radicals will result in a lengthening of the chain by $z$ monomer units when a dead chain is formed. We can therefore write the following expression for the instantaneous rate of production of dead chains of degree of polymerization $i$:

$$\frac{\mathrm{d}\hat{P}_i}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathrm{M}]R_{1,i} + \varrho_{\mathrm{re}}R_{1,i-1} + \varrho_{\mathrm{A}}R_{1,i-z} \quad (10)$$

The symbol $\hat{P}_i$ denotes the cumulative CLD. The instantaneous CLD will be referred to as $P_i$.

$$\mathrm{P}_i \equiv \frac{\mathrm{d}\hat{P}_i}{\mathrm{d}t} \quad (11)$$

**B. Analytical Solution.** For an initial examination of the form of the radical chain-length distribution, more insight can be gained by working with the equivalent of eqs 2–10 in integral form, i.e., by treating the $R_i$ as a continuous function of the degree of polymerization. Russell et al.[18] have given a justification of the validity of this treatment. The populations $R_{1,i}$ are now replaced by $R_1(N)$ where $N$ is the continuous degree of polymerization.

The change to continuous variables allows the following identity to be used

$$k_{\mathrm{p}}^{i}R_{1,i} - k_{\mathrm{p}}^{i-1}R_{1,i-1} = \frac{k_{\mathrm{p}}^{i}R_{1,i} - k_{\mathrm{p}}^{i-1}R_{1,i-1}}{i - (i-1)} = \frac{\Delta k_{\mathrm{p}}^{i}R_{1,i}}{\Delta i} = \frac{\partial k_{\mathrm{p}}(N)R_1(N)}{\partial N} \quad (12)$$

We can therefore write (if $k_{\mathrm{p}}$ is independent of degree of polymerization)

$$\frac{\partial R_1(N)}{\partial t} = -\varrho R_1(N) - k_{\mathrm{tr}}[\mathrm{M}]R_1(N) - [\mathrm{M}]\frac{\partial k_{\mathrm{p}}R_1(N)}{\partial N},\ N > z \quad (13)$$

or, more generally,

$$\frac{\partial R_1(N,t)}{\partial t} = -\varrho R_1(N) - k_{\mathrm{tr}}[\mathrm{M}]R_1(N) - [\mathrm{M}]\frac{\partial k_{\mathrm{p}}(N)R_1(N)}{\partial N},\ N > z \quad (14)$$

The RCLD for chains longer than $z$ can be found by integrating the steady-state (in time) solution of eq 13 from $z$ to $N$, assuming that $k_{\mathrm{p}}$ is independent of degree of polymerization:

$$R_1(N) = R_1(z)\exp\left[\frac{-(\varrho + k_{\mathrm{tr}}[\mathrm{M}])}{k_{\mathrm{p}}[\mathrm{M}]}(N - z)\right],\ N > z \quad (15)$$

As the value of $z$ is normally small ($z \ll N$, for most $N$), it is possible to simplify eq 15 further:

$$R_1(N) = R_1(z)\exp\left[\frac{-(\varrho + k_{\mathrm{tr}}[\mathrm{M}])}{k_{\mathrm{p}}[\mathrm{M}]}N\right],\ N > z \quad (16)$$

Equation 16 describes the RCLD well for all but the smallest chains. We can therefore write an expression for the instantaneous rate of production of dead chains of degree of polymerization $N$:

$$\frac{\partial \hat{P}(N)}{\partial t} = k_{\mathrm{tr}}[\mathrm{M}]R_1(N) + \varrho_{\mathrm{re}}R_1(N-1) + \varrho_{\mathrm{A}}R_1(N-z) \tag{17}$$

To simplify eq 17, we realize that for most values of $N$ for a particular polymer $N \gg 1, z$ and therefore the terms $R(N-1)$ and $R(N-z)$ can be replaced by $R(N)$. We here include this simplification for conceptual clarity but note that in simulations performed with computer it is unnecessary.

When $N \gg z$ (which is most of the distribution), the form of the CLD is given by

$$\frac{\partial \hat{P}(N)}{\partial t} \equiv P(N) = (k_{\mathrm{tr}}[\mathrm{M}] + \varrho)R_1(z) \exp\left[\frac{-(\varrho + k_{\mathrm{tr}}[\mathrm{M}])}{k_{\mathrm{p}}[\mathrm{M}]}N\right] \tag{18}$$

Stated in another manner, a plot of ln $P(N)$ versus $N$ would have a slope of $-(\varrho + k_{\mathrm{tr}}[\mathrm{M}])/k_{\mathrm{p}}[\mathrm{M}]$. A complicating factor is that [M] changes during the course of a polymerization due to the conversion of monomer into polymer. Furthermore, $\varrho$ is dependent upon $\bar{n}$ (through $\varrho_{\mathrm{re}}$) and $[\mathrm{M}_{\mathrm{aq}}]$, the aqueous phase concentration of monomer (through $\varrho_{\mathrm{I}}$). Therefore the value of the slope of a ln $P(N)$ versus $N$ plot will change during the course of a polymerization. For the case in which $\varrho \to 0$, the slope of the above-mentioned plot would be independent of time (and also conversion) and equal to $-(k_{\mathrm{tr}}/k_{\mathrm{p}})$.

It is also worthwhile at this point to give the equivalent of eq 18 for the case in which a chain-transfer agent, A, with a transfer rate coefficient of $k_{\mathrm{tr,A}}$ is added.

$$\frac{\partial \hat{P}(N)}{\partial t} \equiv P(N) = (\varrho + k_{\mathrm{tr}}[\mathrm{M}] + k_{\mathrm{tr,A}}[\mathrm{A}])R_1(z) \exp\left[\frac{-(\varrho + k_{\mathrm{tr}}[\mathrm{M}] + k_{\mathrm{tr,A}}[\mathrm{A}])}{k_{\mathrm{p}}[\mathrm{M}]}N\right] \tag{19}$$

As can be seen from eq 19, the introduction of a chain-transfer agent other than monomer results in an equation for the CLD that is no more complicated than without the transfer agent: one simply replaces the term $k_{\mathrm{tr}}[\mathrm{M}]$ with $k_{\mathrm{tr}}[\mathrm{M}] + k_{\mathrm{tr,A}}[\mathrm{A}]$.

The form of eqs 18 and 19 shows that the instantaneous number MWD, $P(M)$, produced a zero−one system should be a single-exponential distribution. The distribution has this form because all chain-stopping events are independent of chain length. The single-exponential nature of the instantaneous number MWD means that the polydispersity, the ratio of the weight- to number-average molecular weight ($\langle M_{\mathrm{w}}\rangle/\langle M_{\mathrm{n}}\rangle$), of polymer produced at any moment is 2. The number- and weight-average molecular weights for the instantaneously formed polymer are defined as

$$\langle M_{\mathrm{w}}\rangle = \frac{\int_1^\infty M^2 P(M)}{\int_1^\infty MP(M)} \tag{20}$$

$$\langle M_{\mathrm{n}}\rangle = \frac{\int_1^\infty MP(M)}{\int_1^\infty P(M)} \tag{21}$$

When the cumulative distribution, $\hat{P}(M)$, is considered, the distribution will be a sum of exponentials and therefore the polydispersity of the cumulative distribution, found by replacing $P$ with $\hat{P}$ in eqs 20 and 21, will be greater than or equal to 2.

For most modeling purposes, the approximations made to obtain eq 18 are quite accurate. This is particularly true if size exclusion chromatography (SEC) is used to measure the MWD as this technique is less sensitive at the molecular weights of oligomeric species, precisely the region of the MWD that is affected by the assumptions made in arriving at eq 18.

An important consequence of the form of eq 18 is that experimental MWDs (when plotted as ln $\hat{P}(M)$ vs $M$) of zero−one systems should be either straight lines (if $\varrho$ is small) or, more probably, concave up at low molecular weights and approaching a straight line for large molecular weights; this latter type of MWD is due to polymer produced at different stages of the polymerization having different instantaneous MWDs. However, there is experimental evidence due to Whang et al.[28] which shows a distinct maximum in the plot of ln $\hat{P}(M)$ vs $M$, which they attributed to termination caused by coagulative nucleation. That explanation is consistent with this work. Future work is planned to include the possibility of coagulative nucleation in the kinetic scheme presented above.

## 3. Zero−One−Two Systems

We now turn our attention to an extension of the zero−one system that allows for the fact that termination is not in general instantaneous once entry occurs into a particle already containing a free radical. In this system a particle can contain zero, one, or two radicals. As will be shown this greatly increases the complexity of the system, and no simple solution is possible. It should also be noted that there is no mechanism in this model that prevents a particle from containing three or more free radicals. The model is therefore only applicable when the rate of entry is significantly less than the rate of termination but the termination is not instantaneous.

Other workers[9,13] have already examined the zero−one−two emulsion polymerization system for the case where termination between two radicals in a particle is independent of the length of those radicals. In this work we include chain-length-dependent termination as well as a more realistic, but by no means completely accurate, treatment of desorption and entry. Previous work on this system has allowed all radicals the possibility of exiting (desorbing) from a particle, but this approach can easily be seen to be physically incorrect due to the essentially zero solubility of large organic molecules in the aqueous phase. In fact, only the very smallest radicals, those created by transfer, have any appreciable solubility in the aqueous phase. Therefore only these small radicals could possibly desorb from a latex particle.

It will be seen that including such phenomena as chain-length-dependent termination and a physically realistic picture of desorption greatly increases the computational power required to determine a numerical solution and that no simple relationship equivalent to eq 18 for the zero−one case can be obtained. The equations describing the RCLD and MWD are given here, without numerical solution, to establish the minimum level of detail that is required in the modeling of such systems.

**Equations Describing Radical Chain-Length Distribution and Molecular Weight Distribution.** The kinetic processes which must be included in the analysis of the zero–one–two systems are outlined below. Some approximations and simplifications have been included in the model presented here, but this has only been done to simplify the equations presented below. If a numerical solution of these equations were to be performed, then the extra detail could be included with negligible increase in computational time or difficulty. These kinetic processes are

(i) Entry, which is here assumed to be of monomeric species. The fact that entering species (particularly those derived from initiator decomposition) are generally larger than monomeric species has been neglected in keeping with the aims presented above.

(ii) Desorption of monomeric radicals. Unlike in the zero–one system discussed above, for the zero–one–two system all entering species are taken to be monomeric and therefore the possibility of initiator-derived radicals desorbing is included in this system. Again, this is done for simplification, and a more rigorous treatment should take into account that only those radicals created by transfer reactions can desorb from the latex particles.

(iii) Propagation. This is straightforward, the rate of propagation in particles with two radicals being just twice the rate in particles with one radical.

(iv) Transfer to monomer, by which a radical becomes a dead chain and a monomeric radical is created from monomer.

(v) Termination between two radicals in a particle which depends on the volume of the particle and their diffusion coefficients, which are in turn dependent on the size of the radical chains.

We distinguish particles according to the number of radicals they contain and define the populations $R_0$, $R_1$, and $R_2$ as the fraction of particles with zero, one, and two radicals, respectively. The $R_1$ and $R_2$ particles are further distinguished on the basis of the length of the radical(s) contained therein. We therefore define $R_1(N)$ as the fraction of particles containing an $N$-meric radical and $R_2(N,N')$ as the fraction of particles containing an $N$-meric radical and an $N'$-meric radical, where $N' \le N$. Up until this point, the treatment presented here is equivalent to the doubly-distinguished distribution of Lichti et al.[9] However, it is necessary to further subdivide the $R_1(N)$ particles into $R_1(1)$ and $R_1(N)$, where $N > 1$, because of the fact that only monomeric radicals can desorb, and to subdivide the $R_2(N,N')$ particles into $R_2(1,1)$ and $R_2(N,1)$, where $N > 1$, and $R_2(N,N')$, where $N \ge N' > 1$, for the same reason.

It should be noted that we have written the equations below in terms of degrees of polymerization that are continuous, as was done for the zero–one system. This has been done without writing the discrete equations to enable us to keep the notation clear. The evolution equations are

$$\frac{\mathrm{d}R_0}{\mathrm{d}t} = k_{\mathrm{dM}}R_1(1) - \varrho R_0 + \int_1^\infty\int_1^\infty c(N,N')R_2(N,N')\mathrm{d}N'\mathrm{d}N \quad (22)$$

$$\frac{\mathrm{d}R_1(1)}{\mathrm{d}t} = \varrho R_0 + 2k_{\mathrm{dM}}R_2(1,1) + k_{\mathrm{tr}}[\mathrm{M}]\int_1^\infty R_1(N)\mathrm{d}N - k_{\mathrm{tr}}[\mathrm{M}]R_1(1) - \varrho R_1(1) - k_{\mathrm{p}}[\mathrm{M}]R_1(1) - k_{\mathrm{dM}}R_1(1) \quad (23)$$

$$\frac{\mathrm{d}R_1(N)}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{M}]R_1(N-1) + k_{\mathrm{dM}}R_2(N,1) - \varrho R_1(N) - k_{\mathrm{p}}[\mathrm{M}]R_1(N) - k_{\mathrm{tr}}[\mathrm{M}]R_1(N) \quad (24)$$

$$\frac{\mathrm{d}R_2(1,1)}{\mathrm{d}t} = \varrho R_1(1) + k_{\mathrm{tr}}[\mathrm{M}]\int_1^\infty R_2(N,1)\mathrm{d}N - k_{\mathrm{tr}}[\mathrm{M}]R_2(1,1) - c(1,1)R_2(1,1) - 2k_{\mathrm{p}}[\mathrm{M}]R_2(1,1) - 2k_{\mathrm{dM}}R_2(1,1) \quad (25)$$

$$\frac{\mathrm{d}R_2(N,1)}{\mathrm{d}t} = \varrho R_1(N) + k_{\mathrm{tr}}[\mathrm{M}]\int_1^N R_2(N,N')\mathrm{d}N' + k_{\mathrm{tr}}[\mathrm{M}]\int_N^\infty R_2(N',N)\mathrm{d}N' - 2k_{\mathrm{tr}}[\mathrm{M}]R_2(N,1) - k_{\mathrm{dM}}R_2(N,1) - 2k_{\mathrm{p}}[\mathrm{M}]R_2(N,1) - c(N,1)R_2(N,1) \quad (26)$$

$$\frac{\mathrm{d}R_2(N,N')}{\mathrm{d}t} = 2k_{\mathrm{p}}[\mathrm{M}]R_2(N-1,N'-1) - 2k_{\mathrm{p}}[\mathrm{M}]R_2(N,N') - 2k_{\mathrm{tr}}[\mathrm{M}]R_2(N,N') - c(N,N')R_2(N,N') \quad (27)$$

The rate parameters in eqs 22–27 are the same as those used for zero–one systems. The pseudo-first-order termination rate coefficient for termination between two radicals with degrees of polymerization $N$ and $N'$ is given by $c(N,N')$ and related to $k_t$ by the expression

$$c(N,N') = \frac{k_{\mathrm{t}}(N,N')}{N_{\mathrm{A}}V_{\mathrm{s}}} \quad (28)$$

where $V_s$ is the swollen volume of a latex particle.

Equations 22–27 are exact within the confines of the mechanistic assumptions made in points i–v above. To further simplify the system, the steady-state assumption can be made. This assumption will not be valid at the beginning of the reaction when the average number of radicals per particle is rapidly increasing, i.e., during the approach to steady-state conditions. In practice this time is short compared to the time over which dead polymer is produced and the full time-dependent solutions of eqs 22–27 are unnecessary. Furthermore, the rate of production of dead polymer during the approach to steady state is also lower than during the steady state thereby ensuring that the steady-state approximation is well justified. One then has

$$R_0 = \frac{k_{\mathrm{dM}}R_1(1) + \int_1^\infty\int_1^\infty c(N,N')R_2(N,N')\mathrm{d}N'\mathrm{d}N}{\varrho} \quad (29)$$

$$R_1(1) = \frac{\varrho R_0 + 2k_{\mathrm{dM}}R_2(1,1) + k_{\mathrm{tr}}[\mathrm{M}]\int_1^\infty R_1(N)\mathrm{d}N}{\varrho + k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{dM}}} \quad (30)$$

$$R_1(N) = \frac{k_{\mathrm{p}}[\mathrm{M}]R_1(N-1) + k_{\mathrm{dM}}R_2(N,1)}{\varrho + k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}]}, N > 1 \quad (31)$$

$$R_2(1,1) = \frac{\varrho R_1(1) + k_{\mathrm{tr}}[\mathrm{M}]\int_1^\infty R_2(N,1)\mathrm{d}N}{c(1,1) + 2k_{\mathrm{p}}[\mathrm{M}] + 2k_{\mathrm{dM}}} \quad (32)$$

$$R_2(N,1) = [\varrho R_1(N) + k_{\mathrm{tr}}[\mathrm{M}]\int_1^N R_2(N,N')\mathrm{d}N' + k_{\mathrm{tr}}[\mathrm{M}]\int_N^\infty R_2(N',N)\mathrm{d}N']/[k_{\mathrm{dM}} + 2k_{\mathrm{p}}[\mathrm{M}] + 2k_{\mathrm{tr}}[\mathrm{M}] + c(N,1)],\quad N > 1 \quad (33)$$

$$R_2(N,N') = \frac{2k_{\mathrm{p}}[\mathrm{M}]R_2(N-1,N'-1)}{2k_{\mathrm{p}}[\mathrm{M}] + 2k_{\mathrm{tr}}[\mathrm{M}] + c(N,N')},\quad N \geq N' > 1 \quad (34)$$

The CLD (or MWD) is found from the rate of formation of dead chains in $R_1$ and $R_2$ particles. These events are transfer in the $R_1$ particles and transfer and termination, by both combination and disproportionation, in the $R_2$ particles.

$$\frac{\mathrm{d}\hat{P}(1)}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathrm{M}]R_1(1) + 2k_{\mathrm{tr}}[\mathrm{M}]R_2(1,1) + \int_2^\infty k_{\mathrm{tr}}[\mathrm{M}]R_2(N,1)\mathrm{d}N \quad (35)$$

$$\frac{\mathrm{d}\hat{P}(N)}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathrm{M}]R_1(N) + \int_1^N (k_{\mathrm{tr}}[\mathrm{M}] + c_{\mathrm{d}}(N,N'))R_2(N,N')\mathrm{d}N' + \int_N^\infty (k_{\mathrm{tr}}[\mathrm{M}] + c_{\mathrm{d}}(N,N'))R_2(N',N)\mathrm{d}N' + \int_1^{N-1} c_{\mathrm{c}}(N',N-N') R_2(N',N-N')\mathrm{d}N' \quad (36)$$

Here the symbols $c_{\mathrm{c}}$ and $c_{\mathrm{d}}$ are pseudo-first-order termination rate coefficients for combination and disproportionation, respectively.

One means of solving eqs 29–34 is to convert them to the equivalent finite difference equations, which comprise an infinite set of linear simultaneous equations. A further means of simplifying the solution of these equations is truncation,[18] which takes into account that polymer is not formed beyond some large but finite molecular weight. A second technique which might be employed to enable this set of equations to be solved is coarse-graining,[18] which involves grouping radicals that behave in a kinetically similar manner. This procedure was not implemented here. The essentials of the MWD for a zero–one–two system will be intermediate between those of a zero–one and a pseudobulk system, which are treated in detail in the preceding and following sections.

## 4. Pseudobulk and Bulk Systems

The equations presented in this section are applicable to free-radical polymerization systems in which compartmentalization of radicals does not occur or is unimportant. Such systems include bulk, solution, dispersion, and suspension polymerizations and emulsion polymerizations in which the average number of radicals in each individual locus of polymerization is high or in which compartmentalization is unimportant.

***A. Equations Describing Radical Chain-Length* Distribution and Molecular Weight Distribution.** As it forms the basis for this work, we here describe the model of Russell et al.[18] in a condensed form. The reader is referred to this earlier work for further detail. The current work employs slightly different notation from Russell et al. and is more consistent with that employed by other workers in this field.[8,12,29] For the population of radicals of degree of polymerization $i$, we use $R_i$ rather than $T_i$, and for the population of dead polymer of degree of polymerization $i$, we use $P_i$.

Following the example of Russell et al., we can write the following equations for the time evolution of $R_i$, the population of radicals with degree of polymerization $i$:

$$\frac{\mathrm{d}R_1}{\mathrm{d}t} = \varrho + k_{\mathrm{tr}}[\mathrm{M}]\sum_{j=2}^{\infty} R_j - k_{\mathrm{p}}{}^{1}[\mathrm{M}]R_1 - \beta k_{\mathrm{tr}}[\mathrm{M}]\sum_{j=2}^{\infty} R_j - 2R_1\sum_{j=1}^{\infty} c_{1j}R_j \quad (37\mathrm{a})$$

$$\frac{\mathrm{d}R_1}{\mathrm{d}t} = 2fk_{\mathrm{d}}[\mathrm{I}] + k_{\mathrm{tr}}[\mathrm{M}]\sum_{j=2}^{\infty} R_j - k_{\mathrm{p}}{}^{1}[\mathrm{M}]R_1 - 2R_1\sum_{j=1}^{\infty} k_{\mathrm{t}}{}^{1j}R_j \quad (37\mathrm{b})$$

$$\frac{\mathrm{d}R_i}{\mathrm{d}t} = k_{\mathrm{p}}{}^{i-1}[\mathrm{M}]R_{i-1} - k_{\mathrm{p}}{}^{i}[\mathrm{M}]R_i - k_{\mathrm{tr}}[\mathrm{M}]R_i - 2R_i\sum_{j=1}^{\infty} c_{ij}R_j \quad (38\mathrm{a})$$

$$\frac{\mathrm{d}R_i}{\mathrm{d}t} = k_{\mathrm{p}}{}^{i-1}[\mathrm{M}]R_{i-1} - k_{\mathrm{p}}{}^{i}[\mathrm{M}]R_i - k_{\mathrm{tr}}[\mathrm{M}]R_i - 2R_i\sum_{j=1}^{\infty} k_{\mathrm{t}}{}^{ij}R_j \quad (38\mathrm{b})$$

The equations labeled "a" above are for heterogeneous (emulsion, suspension, or dispersion) systems and the $R_i$ are number concentrations per particle, whereas those labeled "b" are for homogeneous (bulk or solution) systems and the $R_i$ are molar concentrations. Note that the equations for the emulsion system are always true when the number of free radicals per particle, $\bar{n}$, is significantly greater than 0.5 and also when radicals rapidly re-enter and re-escape and intraparticle termination is rate-determining (limit 3 of Casey et al.[27]).

The termination rate coefficient for termination between two macroradicals of length $i$ and $j$ is given by $c_{ij}$ for the case of heterogeneous polymerizations and by $k_{\mathrm{t}}{}^{ij}$ for homogeneous polymerizations. The termination rate coefficients for the two cases are related by the expression

$$c_{ij} = \frac{k_{\mathrm{t}}{}^{ij}}{N_{\mathrm{A}}V_{\mathrm{s}}} \quad (39)$$

which is the discrete equivalent of eq 28.

In eq 37b, the rate of creation of radicals from initiator is given by $2fk_{\mathrm{d}}[\mathrm{I}]$, where $f$ is the initiator efficiency, $k_{\mathrm{d}}$ is the dissociation rate of the initiator, and [I] is the concentration of the initiator. Note that as eq 37b is written it assumes that each dissociation event involving initiator creates two radicals that can initiate polymerization. For initiator where this is not the case, eq 37b must be trivially altered. It should also be realized that in emulsion polymerizations the entering species are not all monomeric. This feature of the model will be included at a later stage when exact numerical calculations are made.

For the number of free radicals per particle, $\bar{n}$, and the corresponding quantity for bulk polymerizations,

[R], the total concentration of radicals is given by

$$\sum_{i=1}^{\infty} R_i = \bar{n} \qquad (40a)$$

$$\sum_{i=1}^{\infty} R_i = [\mathrm{R}] \qquad (40b)$$

and related by the expression

$$\bar{n} = [\mathrm{R}] N_{\mathrm{A}} V_{\mathrm{s}} \qquad (41)$$

Equation 38 may be solved to find the $R_i$ (for $i > 1$) by application of the steady-state assumption for the $R_i$, giving

$$R_i = \frac{k_{\mathrm{p}}^{i-1}[\mathrm{M}]R_{i-1}}{k_{\mathrm{p}}^{i}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}] + 2\sum_{j=1}^{\infty} c_{ij} R_j} \qquad (42a)$$

$$R_i = \frac{k_{\mathrm{p}}^{i-1}[\mathrm{M}]R_{i-1}}{k_{\mathrm{p}}^{i}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}] + 2\sum_{j=1}^{\infty} k_{\mathrm{t}}^{ij} R_j} \qquad (42b)$$

An important feature of eqs 42 is that the $R_i$ are strongly coupled to each other. Any analytic solution therefore must involve a simplifying assumption that removes this coupling. Conversely, it is possible to solve for the $R_i$ by an iterative numerical procedure. Such techniques will be discussed in the section Approximate Analytical Solutions.

Once a solution for the $R_i$ has been obtained, by whatever means, the RCLD can be found from the rate of chain-stopping events. These are transfer to monomer and termination, by both combination and disproportionation. The rate of production of dead polymer of degree of polymerization $i$ is then given by

$$\frac{\mathrm{d}\hat{P}_i}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathrm{M}]R_i + 2\sum_{j=1}^{i-1} c^{\mathrm{c}}{}_{j,i-j} R_j R_{i-j} + 2R_i \sum_{j=1}^{\infty} c^{\mathrm{d}}{}_{i,j} R_j \qquad (43a)$$

$$\frac{\mathrm{d}\hat{P}_i}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathrm{M}]R_i + 2\sum_{j=1}^{i-1} k_{\mathrm{tc}}{}^{j,i-j} R_j R_{i-j} + 2R_i \sum_{j=1}^{\infty} k_{\mathrm{td}}{}^{i,j} R_j \qquad (43b)$$

**B. Approximate Analytic Solutions.** As was done for the case of a zero–one system, for our initial examination of the form of the RCLD we will examine the equivalent of eqs 37–38 in integral form, i.e., by treating the $R_i$ as a continuous function of the degree of polymerization. As previously stated, Russell et al.[18] have given a justification of the validity of this treatment. To effect this change, the populations $R_i$ are now replaced by $R(N)$ where $N$ is the continuous degree of polymerization and $k_{\mathrm{t}}^{ij}$ and $c_{ij}$ are replaced by $k_{\mathrm{t}}(N,N')$ and $c(N,N')$, respectively.

The change to continuous variables allows the following identity to be used

$$k_{\mathrm{p}}^{i}R_i - k_{\mathrm{p}}^{i-1}R_{i-1} = \frac{k_{\mathrm{p}}^{i}R_i - k_{\mathrm{p}}^{i-1}R_{i-1}}{i - (i-1)} = \frac{\Delta(k_{\mathrm{p}}^{i}R_i)}{\Delta i} = \frac{\partial k_{\mathrm{p}}(N)R(N)}{\partial N} \qquad (44)$$

We can therefore rewrite eqs 38 as

$$\frac{\partial R(N)}{\partial t} = -k_{\mathrm{tr}}[\mathrm{M}]R(N) - [\mathrm{M}]\frac{\partial k_{\mathrm{p}}(N)R(N)}{\partial N} - 2R(N)\int_1^{\infty} c(N,N')R(N')\mathrm{d}N', \; N > 1 \qquad (45a)$$

$$\frac{\partial R(N)}{\partial t} = -k_{\mathrm{tr}}[\mathrm{M}]R(N) - [\mathrm{M}]\frac{\partial k_{\mathrm{p}}(N)R(N)}{\partial N} - 2R(N)\int_1^{\infty} k_{\mathrm{t}}(N,N')R(N')\mathrm{d}N', \; N > 1 \qquad (45b)$$

Without loss of accuracy, the $R(N)$ can be assumed to be in a pseudo-steady-state. Once the steady-state approximation has been made in eq 45, rearrangement followed by integration from 1 to $N$ and putting $k_{\mathrm{p}}$ independent of $N$ gives the following expressions for $R(N)$:

$$R(N) = R(1)\exp\left[\frac{-k_{\mathrm{tr}}[\mathrm{M}](N-1) - 2\int_1^{N}\int_1^{\infty} c(N'',N')R(N')\mathrm{d}N'\mathrm{d}N''}{k_{\mathrm{p}}[\mathrm{M}]}\right], \; N > 1 \qquad (46a)$$

$$R(N) = R(1)\exp\left[\frac{-k_{\mathrm{tr}}[\mathrm{M}](N-1) - 2\int_1^{N}\int_1^{\infty} k_{\mathrm{t}}(N'',N')R(N')\mathrm{d}N'\mathrm{d}N''}{k_{\mathrm{p}}[\mathrm{M}]}\right], \; N > 1 \qquad (46b)$$

The quantity $R(1)$ can be found by making the steady-state approximation in the continuous form of eqs 37, but its actual value is unimportant for the purpose of examining the qualitative form of $R(N)$.

Equations 46 are nonlinear integral equations and as such have no simple solution. They have this form due to the strongly coupled nature of the radical populations, because radicals of a particular length can terminate with radicals of all other chain lengths, and therefore each $R(N)$ depends upon the values of $R(N)$ for all other $N$.

There have been a number of inferences in the literature about termination in free-radical kinetics from experimental and theoretical studies of diffusion.[30] While termination is diffusion-controlled, it has been shown[18] that kinetically important diffusion in systems where termination is occurring is, for all except glassy systems, dominated by the mutual diffusion between very short chains and relatively long (entangled) ones, for which there is a scarcity of diffusion coefficient data.

For intermediate conversions, the rate-determining step in termination processes is center-of-mass diffusion.[18] Therefore we can define the termination rate coefficient as in the Smoluchowski equation:

$$k_{\mathrm{t}}(N,N') = 2\pi p(r(N) + r(N'))D(N,N')N_{\mathrm{A}} \qquad (47)$$

where $(r(N) + r(N'))$ is the radius of interaction for termination which is taken to be independent of $N$ and $N'$ and set equal to $\sigma$, the Lennard–Jones diameter of a monomer unit. The use of $\sigma$ for the radius of interaction for termination has been extensively justified by Russell et al.[19] This justification is reproduced here in a condensed form as its basis may not be immediately apparent. First consider the reaction between two monomeric radicals. The interaction distance for such a case is obviously well approximated by $\sigma$. Next consider termination between a monomeric radical and a long radical. The motion of the small radical will be so rapid that the long chain can be thought of as essentially immobile. Therefore reaction will occur only when the small radical diffuses within a small distance of the *radical site* on the end of the long chain. This distance will again be approximately $\sigma$. For the case of two long radicals, the same argument holds. Reaction can only occur when the radical sites (not the chains) are within a small distance, approximately $\sigma$, of each other. Two more widely separated radicals, even if their coils are entangled and especially so for relatively concentrated polymer systems, are not destined to react. It should be remembered here that, although the literature contains a considerable number of experimental and theoretical results for center-of-mass diffusion of long chains,[30] what is important for termination is the diffusion and reaction of relatively short chains.

It should be pointed out that there is some disagreement here between experimental and theoretical results. This is further complicated by the fact that current theory only deals with the situation in which both chains are long and of the same length, whereas in real polymerization systems the most kinetically significant event is termination between a short and a long chain. For the situation in which both chains are long and of the same length, theory[31-35] suggests that $k_t \sim N^{-3/2}$. This result occurs due to what de Gennes[33] called "compact exploration" which results in the radius of interaction appearing to be $R$, the radius of gyration, rather than $\sigma$, and thereby resulting in a weaker dependence of $k_t$ upon chain length than we have used in this work. The situation is further complicated by the fact that experimental evidence on this point is difficult to obtain. Tulig and Tirrell[1] have presented data which indicates that $\langle k_t \rangle$ varies as the inverse square of the average degree of polymerization, although they suggest that the sparsity of data precludes making any strong conclusions. In light of the above we have chosen to use $\sigma$ rather than $R$ for the radius of interaction because (1) for reasons expounded in the previous paragraph we believe that $\sigma$ gives the correct radius of interaction for reaction between a short and a long chain and (2) the use of $\sigma$ for the radius of interaction gives the experimentally observed dependence of $k_t$ upon chain length ($k_t \sim N^{-2}$).

In eq 47, $p$ is a reaction probability with a value between 0.25 and 1 which takes into account that the radicals have spin $\pm^1/_2$,[19] and $D(N,N')$ is the mutual diffusion coefficient for the radical ends of an $N$-mer and an $N'$-mer, which can be partitioned into a sum of contributions from the two species

$$D(N,N') = D(N) + D(N') \qquad (48)$$

Russell et al.[18] have argued that only the longest length scale motions determine the rate of termination. These motions are the center-of-mass diffusion of the chain as a whole, $D_{com}(N)$, and growth of the chain end by propagation, known as 'reaction diffusion', $D_{rd}(N)$. Hence:

$$D(N) = D_{com}(N) + D_{rd}(N) \qquad (49)$$

where

$$D_{rd}(N) = {}^1/_6 k_p[M]a^2 \qquad (50)$$

and $a$ is the root-mean-square end-to-end distance per square root of the number of monomer units in a polymer chain. Equation 50 is independent of chain length except for the dependence of $k_p$ upon chain length for the shortest chains, which can be ignored because for these chains center-of-mass diffusion will be much faster than reaction diffusion. We can therefore replace $D_{rd}(N)$ by $D_{rd}$.

The exact form of the center-of-mass diffusion of polymeric species is the topic of considerable debate. At very low concentrations of polymer, $D_{com}(N)$ would be expected by vary inversely as the size of a small radical and therefore to scale as the inverse square root of the degree of polymerization according to a Stokes–Einstein argument. There is also evidence[36] that indicates that at intermediate polymer concentrations $D_{com}(N)$ scales as the inverse of the chain length. For long chains at medium to high polymer concentrations, there is much theoretical and experimental evidence that suggests that chains diffuse by reptation[37] and that $D_{com}(N)$ is therefore proportional to the inverse square of the chain length.[38] There is even experimental evidence that $D_{com}(N)$ may be inversely proportional to powers of the chain length that are greater than 2.[36] In light of this we write a general expression for $D_{com}(N)$ in terms of a parameter, $\alpha$, that may depend on both chain length, $N$, and the weight fraction of polymer in the locus of polymerization, $w_p$.

$$D_{com}(N,w_p) = \frac{D_{mon}(w_p)}{N^{\alpha(N,w_p)}} \qquad (51)$$

In eq 51, $D_{mon}(w_p)$ is the diffusion coefficient of monomer at a given $w_p$. The specification of the exact form of $\alpha$ used in the examination of model systems will be given when such systems are examined.

We now wish to examine the form of the RCLD which occurs with the model for termination rate coefficients given above. Before this can be achieved, it is useful to define an average rate coefficient for termination, $\langle k_t \rangle$, and an average diffusion coefficient, $\bar{D}$. Both these averages are weighted according by the radical distribution function, $R(N)$, and therefore they depend on the RCLD.

$$\langle k_t \rangle = \frac{\int_1^\infty \int_1^\infty k_t(N,N')R(N)R(N')\mathrm{d}N\mathrm{d}N'}{\int_1^\infty \int_1^\infty R(N)R(N')\mathrm{d}N\mathrm{d}N'} \equiv 4\pi\sigma N_A \bar{D} \qquad (52)$$

where

$$\bar{D} = \frac{\int_1^\infty D(N)R(N)\mathrm{d}N}{\int_1^\infty R(N)\mathrm{d}N} \qquad (53)$$

We can now write an expression for the RCLD.

$$\ln\left(\frac{R(N)}{R(1)}\right) = -\left(\frac{k_{tr}[M]}{k_p[M]}\right)(N-1) - \left(\frac{4\pi\sigma N_A[R]D_{rd}}{k_p[M]}\right)(N-1) - \left(\frac{\langle k_t \rangle [R]}{k_p[M]}\right)(N-1) - \left(\frac{4\pi\sigma N_A D_{mon}[R]}{k_p[M]}\frac{\int_1^N N'^{(-\alpha)}\mathrm{d}N'}{N-1}\right)(N-1),\ N > 1 \qquad (54)$$

Or more simply

$$\ln\left(\frac{R(N)}{R(1)}\right) = -(F_{\mathrm{tr}} + F_{\mathrm{rd}} + F_{\mathrm{term}} + F_{\mathrm{com}}(N))(N - 1), N > 1 \quad (55)$$

The form of eq 54 is most easily understood by realizing that writing diffusion coefficients in the form of eq 48 means that diffusion, or termination, of a particular chain (an $N$-mer) can be separated into two components: one due to the radical in question terminating other radicals (for which the diffusion coefficient of the $N$-mer is important) and the other due to other radicals terminating the radical in question (for which the diffusion coefficients of all other radicals are important). If one adopts this viewpoint, then the terms $F_{\mathrm{rd}}$ and $F_{\mathrm{com}}(N)$ are due to $N$-mers terminating other radicals and the term $F_{\mathrm{term}}$ is due to other radicals terminating $N$-mers.

When $\alpha = 0$, we have the trivial case of chain-length-independent termination and $F_{\mathrm{com}}(N)$ simplifies to $(4\pi\sigma N_{\mathrm{A}}D_{\mathrm{com}}[\mathrm{R}]/k_{\mathrm{p}}[\mathrm{M}])$, where $D_{\mathrm{com}}$ is the chain-length-independent center-of-mass diffusion coefficient for all chain lengths. When $\alpha > 0$ we find that

$$\lim_{N\to\infty}(F_{\mathrm{com}}(N)) = 0 \quad (56)$$

and therefore

$$\lim_{N\to\infty}\left(\frac{\ln R(N)}{N}\right) = -(F_{\mathrm{tr}} + F_{\mathrm{rd}} + F_{\mathrm{term}}) \quad (57)$$

Furthermore,

$$\lim_{N\to\infty}\left(\frac{\ln R(N)}{N}\right) \cong -\left(\frac{k_{\mathrm{tr}}}{k_{\mathrm{p}}} + \frac{\langle k_{\mathrm{t}}\rangle[\mathrm{R}]}{k_{\mathrm{p}}[\mathrm{M}]}\right) \quad (58)$$

if $F_{\mathrm{rd}} \ll F_{\mathrm{tr}}, F_{\mathrm{term}}$.

Equation 58 is very important as it shows that for long chains the distribution of radicals as a function of their length depends upon the concentrations of monomer and total radicals, the rate coefficients for transfer and propagation, and the *average* rate coefficient for termination, all of which are *independent* of chain length. Therefore if $R(N)$ could be measured and a plot of $\ln R(N)$ vs $N$ could be constructed, we would predict that at large values of $N$ the curve so produced would be a straight line with a slope equal to the right-hand side of eq 58.

At this point it is worth looking at the form that eq 58 takes if there is some added chain-transfer agent. In this case we obtain

$$\lim_{N\to\infty}\left(\frac{\ln R(N)}{N}\right) \cong -\left(\frac{k_{\mathrm{tr}}[\mathrm{M}] + k_{\mathrm{tr,A}}[\mathrm{A}] + \langle k_{\mathrm{t}}\rangle[\mathrm{R}]}{k_{\mathrm{p}}[\mathrm{M}]}\right) \quad (59)$$

We now turn our attention to the MWD (or the chain-length distribution). IN a free-radical polymerization system, there are three mechanisms by which dead polymer can be formed, transfer (where the dead chain has the same length as the radical from which it was formed), termination by combination (where the dead polymer formed has a length that is the sum of the lengths of the two radicals from which it was formed), and termination by disproportionation (where two dead chains are formed which have the same lengths as the radicals from which they were derived). One then has the following expressions for the rate of formation of dead polymer of degree of polymerization $N$, $P(N)$.

$$P(N) = \frac{\partial\hat{P}(N)}{\partial t} = k_{\mathrm{tr}}[\mathrm{M}]R(N) + 2\int_1^{N-1} c_{\mathrm{c}}(N',N-N')R(N')R(N-N')\,\mathrm{d}N' + 2R(N)\int_1^{\infty} c_{\mathrm{d}}(N,N')R(N')\,\mathrm{d}N' \quad (60a)$$

$$P(N) = \frac{\partial\hat{P}(N)}{\partial t} = k_{\mathrm{tr}}[\mathrm{M}]R(N) + 2\int_1^{N-1} k_{\mathrm{tc}}(N',N-N')R(N')R(N-N')\,\mathrm{d}N' + 2R(N)\int_1^{\infty} k_{\mathrm{td}}(N,N')R(N')\,\mathrm{d}N' \quad (60b)$$

As written, eqs 60 give the instantaneous rate of production of dead polymer of degree of polymerization $N$. It must be understood that to evaluate the cumulative molecular weight distribution, $\hat{P}(N)$, one must integrate eqs 60 over all experimental time. The most important feature of eqs 60 is that the contribution to the chain-length distribution due to transfer is proportional to $R(N)$ for all $N$ and that the contribution due to disproportionation is proportional to $R(N)$ for large $N$. This means that for a polymerization system in which all termination is by disproportionation, $P(N)$ has the same dependence upon $N$ as $R(N)$ in the limit of infinite chain length.

## 5. Method of Evaluation of the MWD for Pseudobulk Systems

The previous sections dealt with the derivation of the molecular weight distribution in three cases: zero–one, zero–one–two, and pseudobulk or bulk kinetics. This section demonstrates a method of numerically evaluating the MWD for the case of pseudobulk or bulk kinetics.

The first step is to write the steady-state solution of eqs 37 and 38.

$$R_1 = \frac{\varrho\delta_{1z} + k_{\mathrm{tr}}[\mathrm{M}]\bar{n}}{k_{\mathrm{p}}{}^{1}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}] + 2\sum_{j=1}^{\infty} c_{1j}R_j} \quad (61a)$$

$$R_1 = \frac{2fk_{\mathrm{d}}[\mathrm{I}] + k_{\mathrm{tr}}[\mathrm{M}][\mathrm{R}]}{k_{\mathrm{p}}{}^{1}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}] + 2\sum_{j=1}^{\infty} k_{\mathrm{t}}{}^{1j}R_j} \quad (61b)$$

$$R_i = \frac{\varrho\delta_{iz} + k_{\mathrm{p}}{}^{i-1}[\mathrm{M}]R_{i-1}}{k_{\mathrm{p}}{}^{i}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}] + 2\sum_{j=2}^{\infty} c_{ij}R_j} \quad (62a)$$

$$R_i = \frac{k_{\mathrm{p}}{}^{i-1}[\mathrm{M}]R_{i-1}}{k_{\mathrm{p}}{}^{i}[\mathrm{M}] + k_{\mathrm{tr}}[\mathrm{M}] + 2\sum_{j=2}^{\infty} k_{\mathrm{t}}{}^{ij}R_j} \quad (62b)$$

In eqs 61 and 62, we have allowed for a general chain-length dependence of $k_{\mathrm{p}}$ while realizing that $k_{\mathrm{p}}$ will in actuality approach the limiting long-chain value after only a few monomer additions. Also included is the possibility that entering radicals can have a length other than monomeric. In fact, this possibility must be included for consistency with the entry theory of Maxwell et al.[21] which describes the component of entry arising from initiator decomposition. It should also be noted that the possibility of radical desorption does not appear in eq 61a because we have here made the assumption that all desorbed free radicals undergo reentry. Even if this assumption is incorrect, the error introduced should be small as the desorption rate drops rapidly as particle size increases,[22,39] and systems with large particles are those that will be best described by pseudobulk kinetics.

Greater mechanistic understanding of eqs 61 and 62 can be obtained by rewriting the termination term using eq 39 and the discrete equivalents of eqs 47 and 48.

$$R_1 = \frac{\varrho\delta_{1z} + k_{tr}[M]\bar{n}}{k_p^{\,1}[M] + k_{tr}[M] + (4\pi\sigma/V_s)(D_1\bar{n} + \bar{D}\bar{n})} \tag{63a}$$

$$R_1 = \frac{2fk_d[I] + k_{tr}[M][R]}{k_p^{\,1}[M] + k_{tr}[M] + (4\pi\sigma N_A)(D_1[R] + \bar{D}[R])} \tag{63b}$$

$$R_i = \frac{\varrho\delta_{iz} + k_p^{\,i-1}[M]R_{i-1}}{k_p^{\,i}[M] + k_{tr}[M] + (4\pi\sigma/V_s)(D_i\bar{n} + \bar{D}\bar{n})} \tag{64a}$$

$$R_i = \frac{k_p^{\,i-1}[M]R_{i-1}}{k_p^{\,i}[M] + k_{tr}[M] + (4\pi\sigma N_A)(D_i[R] + \bar{D}[R])} \tag{64b}$$

where $\bar{D}$ is an average diffusion coefficient and is defined by the discrete equivalent of eq 53.

The strategy for solving these equations is an iterative one. One guesses the form of the distribution function $R_i$ and a value of $\bar{n}$ (or [R]) and then evaluates $\bar{D}$. The values of $\bar{D}$ and $\bar{n}$ (or [R]) can then be used to obtain new values for the $R_i$ and so on until convergence in the $R_i$ occurs. The problem with this approach is that the number of different values of $i$ for which $R_i$ must be determined is infinite. We here introduce two approximations that are designed to remove this problem: coarse-graining and truncation. Coarse-graining is based upon the realization that radicals whose lengths are approximately equal will behave in ways that are kinetically almost indistinguishable. In eqs 64, only $k_p$ and $D$ depend upon chain length. The case of $k_p$ is trivial as it only varies for very small values of $i$ for which the grain size must be 1 monomer unit. As already discussed, the diffusion coefficient is dependent upon chain length and approaches zero asymptotically as chain length becomes infinite, i.e., $D_i$ varies more slowly as $i$ increases. Therefore it is sensible to have grain sizes that are small (1 monomer unit wide) for small values of $i$ and larger and larger grains as $i$ increases. Obviously the larger the number of grains the better the approximation to the complete equations will be. Truncation involves setting a limit for the length to which a radical can grow or above which the number of chains becomes negligible. The actual value of this upper limit will depend upon the parameter values in eqs 64. This is equivalent to making the final grain of infinite size.

The method of coarse-graining used here is equivalent to replacing sections of the $R_i$ distribution by straight lines and is based upon the following rearrangement of eqs 64.

$$R_{i+b} = R_i \prod_{j=i+1}^{i+b} \left( \frac{k_p[M]}{k_p[M] + k_{tr}[M] + (4\pi\sigma/V_s)(D_j\bar{n} + \bar{D}\bar{n})} \right) \tag{65a}$$

$$R_{i+b} = R_i \prod_{j=i+1}^{i+b} \left( \frac{k_p[M]}{k_p[M] + k_{tr}[M] + (4\pi\sigma N_A)(D_j[R] + \bar{D}[R])} \right) \tag{65b}$$

Here $b$ is an integer which will become the grain size. Equations 65 state that if one knows $\bar{D}$ and $\bar{n}$ and is then given $R_i$ and the appropriate rate coefficients one can calculate $R_{i+b}$. To coarse-grain effectively, one must choose values of $i$ and $b$ such that $D_{i+1} \cong D_{i+b}$ with the added restriction that grain sizes should only be larger than 1 monomer unit when $k_p^{\,i} = k_p$ and when $i > z$. Then one can write

$$R_I = R_{I-1} \left( \frac{k_p[M]}{k_p[M] + k_{tr}[M] + (4\pi\sigma/V_s)(D_I\bar{n} + \bar{D}\bar{n})} \right)^{\Delta_{I-1}} \tag{66a}$$

$$R_I = R_{I-1} \left( \frac{k_p[M]}{k_p[M] + k_{tr}[M] + (4\pi\sigma N_A)(D_I[R] + \bar{D}[R])} \right)^{\Delta_{I-1}} \tag{66b}$$

where $R_I$ is the population of radicals of the first element in grain $I$, $D_I$ is the diffusion coefficient of radicals in grain $I$, $\Delta_{I-1}$ is the number of monomer units between the first element of grain $I$ and the first element of grain $I-1$, and the radicals are of sufficient length that $k_p$ is the long-chain value. The populations $R_I$ defined here are not total populations for all the chain lengths within a grain but just the population of the first element in the grain, and therefore $R_i = R_I = R_{\mathrm{first}(I)}$ where first($I$) is the first element of grain $I$. Truncation is effected by using the following equation

$$R_L = R_{L-1} \left( \frac{k_p[M]}{k_{tr}[M] + (4\pi\sigma/V_s)(D_L\bar{n} + \bar{D}\bar{n})} \right)^{\Delta_{L-1}} \tag{67a}$$

$$R_L = R_{L-1} \left( \frac{k_p[M]}{k_{tr}[M] + (4\pi\sigma N_A)(D_L[R] + \bar{D}[R])} \right)^{\Delta_{L-1}} \tag{67b}$$

where $L$ is the last grain. Radicals can propagate into this grain, but they cannot propagate out of it.

When solving the coarse-grained radical distribution equations, it is important to set up the graining in a way that allows grain size to be readily changed so that the effects of graining upon the resultant distribution can be observed and minimized. In the simulations presented in section 6 of this work, three variables were used to control the graining: the number of grains of width 1 monomer unit, the number of times each grain size greater than 1 monomer unit was repeated, and the degree of polymerization of the first element of the final grain. All grains whose size is greater than 1 monomer unit are of width $2^n$, where $n$ is an integer. It was found that these grains had to be repeated a number of times before $n$ was increased so that the grain size did not grow too rapidly. Initially each of these variables was given a low value which was increased until the distribution no longer changed. For the simulations in this work, the following graining scheme was employed, 240 grains of width 1, each larger grain size was repeated 40 times up to a maximum grain size of 8192 ($2^{13}$) which gave an approximate maximum degree of polymerization at 650 000 and a total of 760 grains.

For convenience sake we rewrite eqs 60, which give the rate of formation of dead polymer from radicals, in terms of discrete variables as

$$\frac{\partial P_i}{\partial t} = P_{i,\mathrm{tr}} + P_{i,\mathrm{tc}} + P_{i,\mathrm{td}} \tag{68}$$

where

$$P_{i,\mathrm{tr}} = k_{\mathrm{tr}}[\mathrm{M}]R_i \tag{69}$$

$$P_{i,\mathrm{tc}} = 2\sum_{j=1}^{i-1} c^{\mathrm{c}}_{j,i-j} R_j R_{i-j} \tag{70a}$$

$$P_{i,\mathrm{tc}} = 2\sum_{j=1}^{i-1} k_{\mathrm{tc}}^{\,j,i-j} R_j R_{i-j} \tag{70b}$$

$$P_{i,\mathrm{td}} = 2R_i\sum_{j=1}^{\infty} c^{\mathrm{d}}_{i,j} R_j \tag{71a}$$

$$P_{i,\mathrm{td}} = 2R_i\sum_{j=1}^{\infty} k_{\mathrm{td}}^{\,i,j} R_j \tag{71b}$$

When evaluating eq 68 it must be remembered that we have only evaluated $R_i$ for certain values of $i$, i.e., when $i$ = first($I$). The term due to transfer, $P_{i,\mathrm{tr}}$, is evaluated trivially as it is proportional to $R_i$. The second term on the right-hand side of eq 68 (the term due to combination), given by eqs 70, is not as straightforward to evaluate. We only want to evaluate $P_{i,\mathrm{tc}}$ for those values of $i$ for which we have evaluated $R_i$. To do this properly involves summing the contribution from all pairs of radicals whose lengths add to give $i$. However, we do not have all this information, only a small subset of it, for those values of $i$ where $i$ = first($I$). The algorithm used to evaluate $P_{i,\mathrm{tc}}$ involves approximating values for $R_j$ and $R_{i-j}$ by the value of $R_I$ for which $i$ or $i-j$ is closest to first($I$) and using information about the size of the grains to avoid determining every product $c^{\mathrm{c}}_{j,i-j}R_jR_{i-j}$ or $k_{\mathrm{td}}^{\,j,i-j}R_jR_{i-j}$. The term $P_{i,\mathrm{td}}$ is simpler to evaluate but employs the same technique as for $P_{i,\mathrm{tc}}$.

## 6. Evaluation of Molecular Weight Distributions in Pseudobulk Polymerizations

**A. Kinetic Parameters for Poly(styrene) and Poly(methyl methacrylate).** Poly(styrene) (PS) and poly(methyl methacrylate) (PMMA) are widely produced and therefore widely studied polymers. Consequently, reliable kinetic parameters are available for these two polymers and the respective monomers. Furthermore, Russell et al.[19] have conducted modeling of the kinetics for these polymers.

For propagation we write

$$\frac{1}{k_{\mathrm{p}}} = \frac{1}{k_{\mathrm{diff}}} + \frac{1}{k_{\mathrm{p}}^{\,0}} \tag{72}$$

to take into account the fact that propagation becomes "diffusion-controlled" at high-conversion. Here $k_{\mathrm{p}}^{0}$ is the "chemically controlled" value of the propagation rate coefficient, which is given by the value of $k_{\mathrm{p}}$ at low weight fraction of polymer, $w_{\mathrm{p}}$, and the diffusion-controlled component, $k_{\mathrm{diff}}$, is given by

$$k_{\mathrm{diff}} = 4\pi\sigma N_{\mathrm{A}}(D_{\mathrm{mon}} + D_{\mathrm{rd}}) \tag{73}$$

The recent realization by Casey et al.[40] that transfer also becomes diffusion-controlled at high weight fraction of polymer is included and given by

$$\frac{1}{k_{\mathrm{tr}}} = \frac{1}{k_{\mathrm{tr}}^{\,0}}\left(\frac{k_{\mathrm{p}}^{\,0}}{k_{\mathrm{diff}}} + 1\right) \tag{74}$$

where $k_{\mathrm{diff}}$ is again given by eq 73.

The values of $k_{\mathrm{p}}^{0}$ for styrene and MMA at 50 °C are taken as 258[41] and 580[42] dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The value of $k_{\mathrm{tr}}^{0} = 9 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ for styrene was taken from the literature value[43] of $k_{\mathrm{tr}}/k_{\mathrm{p}}$, while for MMA $k_{\mathrm{tr}}^{0}$ was taken as $3.3 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$.[44] The values of $\sigma$ = 0.59 nm and $a$ = 0.69 nm[45,46] were employed for MMA, and for styrene we took $\sigma$ = 0.602 nm and $a$ = 0.74 nm.[18,45]

The dependence upon $w_{\mathrm{p}}$ of the diffusion coefficients of styrene in styrene/poly(styrene) systems (eq 75) and MMA in MMA/PMMA systems (eq 76) at 50 °C is that given by Russell et al.[18,47]

$$\log(D_{\mathrm{mon}}/\mathrm{cm}^2\ \mathrm{s}^{-1}) = 0.417 - 29.51w_{\mathrm{p}} + 53.14w_{\mathrm{p}}^{\,2} - 36.03w_{\mathrm{p}}^{\,3}\ \text{(styrene)} \tag{75}$$

$$\log(D_{\mathrm{mon}}/\mathrm{cm}^2\ \mathrm{s}^{-1}) = -4.386 - 3.200w_{\mathrm{p}} + 9.049w_{\mathrm{p}}^{\,2} - 12.079w_{\mathrm{p}}^{\,3}\ \text{(MMA)} \tag{76}$$

Equation 75 is valid only in the range $0.4 \le w_{\mathrm{p}} \le 0.8$, whereas eq 76 is valid for all values of $w_{\mathrm{p}}$ from 0 to 1.

For evaluating entry rate coefficients, the model of Maxwell et al.[21] is employed here.

$$\varrho_{\mathrm{I}} = \frac{2k_{\mathrm{d}}[\mathrm{I}]N_{\mathrm{A}}}{N_{\mathrm{c}}}\left[\frac{2\sqrt{k_{\mathrm{d}}[\mathrm{I}]k_{\mathrm{t}}^{\,\mathrm{aq}}}}{k_{\mathrm{p}}^{\,\mathrm{aq}}[\mathrm{M}_{\mathrm{aq}}]} + 1\right]^{1-z} \tag{77}$$

Here $N_{\mathrm{c}}$ is the number concentration of latex particles, $k_{\mathrm{t}}^{\mathrm{aq}}$ is an average aqueous termination rate constant, $k_{\mathrm{p}}^{\mathrm{aq}}$ is the propagation rate in the aqueous phase (taken to be the same as in the latex phase), [M$_{\mathrm{aq}}$] is the concentration of monomer in the aqueous phase, and $z$ is the critical degree of polymerization at which species irreversibly enter the latex particles. The value of $z$ = 3 was used for styrene, and $z$ = 4 was used for MMA.[19,21,27]

The variation of $D_{\mathrm{com}}(N)$ with chain length used here is also that given by Russell et al.[18]

$$\begin{aligned} D_{\mathrm{com}}(N) &= \frac{D_{\mathrm{mon}}}{N},\ N \le X_{\mathrm{c}} \\ &= \frac{D_{\mathrm{mon}}X_{\mathrm{c}}}{N^2},\ N > X_{\mathrm{c}} \end{aligned} \tag{78}$$

Here $X_{\mathrm{c}}$ is the critical degree of polymerization for onset of the reptational power law for center-of-mass diffusion. This quantity varies with $w_{\mathrm{p}}$, becoming smaller as $w_{\mathrm{p}}$ increases, as given by the relationship

$$X_{\mathrm{c}} = \frac{X_{\mathrm{c}}^{\,0}}{\phi_{\mathrm{p}}} \tag{79}$$

where $\phi_{\mathrm{p}}^{-1} = [d_{\mathrm{p}}/(d_{\mathrm{M}}w_{\mathrm{p}})] + 1 - (d_{\mathrm{p}}/d_{\mathrm{M}})$ and $\phi_{\mathrm{p}}$ is the volume fraction of polymer in the system, $d_{\mathrm{p}}$ is the density of the polymer, and $d_{\mathrm{M}}$ is the density of the monomer. The value of $X_{\mathrm{c}}^{0}$ was taken as an adjustable parameter by Russell et al. and found to have the value

1 for MMA[19] and 4 for styrene.[18] While such values may seem particularly low, the value of $X_c^0 = 1$ for MMA might be taken as indicating that chains of all lengths in the melt are subject to a reptational power law for diffusion. However, further evidence for such a value being adequate to describe diffusion of those small species important in termination kinetics is provided by Piton et al.[48] These workers measured self-diffusion coefficients (equivalent to $D_{\rm com}$ above) for oligomeric ($N = 1, 2, 5$) poly(styrene) analogs as a function of the weight fraction ($0 \le w_p \le 0.6$) of high molecular weight poly(styrene) using the technique of pulsed field gradient $^1$H NMR. They found that the self-diffusion coefficient scaled as $N^{-0.5}$ at $w_p = 0$ and $N^{-1.6}$ at $w_p = 0.6$ with an almost linear dependence of the exponent on polymer weight fraction within this range. The data of Piton et al.[48] show that the functional form represented by eqs 78 and 79 provides a quite adequate representation of the diffusion coefficient of small species obtained experimentally; this however should not be taken as implying that such species undergo reptational diffusion.

In light of the above we have decided to employ a value of $X_c^0 = 1$ for both MMA and poly(styrene). It should be noted that the exact functional dependence of microscopic termination rates on weight fraction (or volume fraction) of polymer depends on both $X_c$ and $D_{\rm mon}$. This model gives adequate agreement ($k_t \sim \phi^{-1.5}$) with direct measurements of termination rates[30] ($k_t \sim \phi^{-1.7}$) obtained from phosphorescence quenching experiments. It should be remembered that these phosphorescence quenching experiments measured termination rates between two long chains, i.e., for an event that is kinetically insignificant in our system, and so exact agreement between our model and such results is not vital (although still desirable).

**B. The Form of the MWD.** We now present predictions for the RCLD and MWD for poly(styrene) and poly(methyl methacrylate) based upon the kinetic scheme of Russell et al.[18] According to arguments presented above, results will generally be presented as plots of ln $R(N)$ or ln $P(N)$ versus $N$. Whang et al.[28] have already made the recommendation that MWDs should be presented in this form so that the kinetic information contained in such plots becomes more accessible. The results which follow lend further weight to this recommendation.

In the work that follows we also give the *number*-average molecular weight, $\langle M_n \rangle$, and *weight*-average molecular weight, $\langle M_w \rangle$, the first and second moments of the molecular weight distribution, $P(M)$. The molecular weight of a polymer chain, $M$, and its degree of polymerization, $N$, are trivially related by the expression $N = M/M_0$, where $M_0$ is the molecular weight of a monomer unit. The polydispersity is $\langle M_w \rangle / \langle M_n \rangle$.

**I. Chain-Length-Independent Termination.** In this work we normally make the assumption that microscopic termination rates are dependent upon the length of the radicals involved. However, it is instructive to examine the form of the MWD that occurs if termination is independent of chain length for a number of reasons. First, it gives a reference point for comparison with the MWD predicted using chain-length-dependent termination rates (given below). Second, for the chain-length-independent case analytic forms exist for $R(N)$ and $P(N)$, and therefore this case serves as a test of our computer code. Third, when polymerization occurs in glassy systems, termination is by reaction diffusion and is therefore independent of chain length.

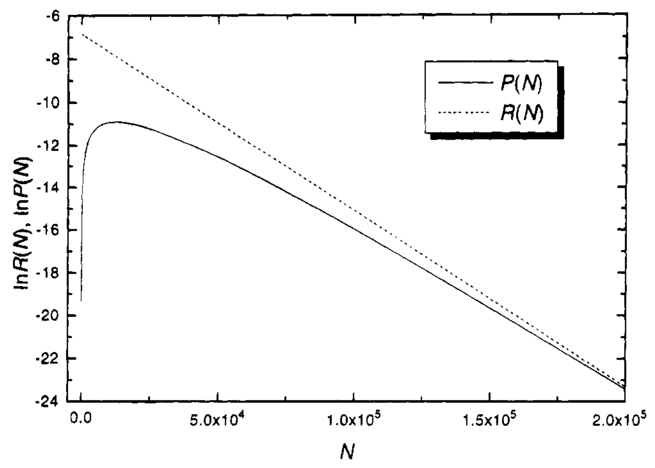

**Figure 1.** Calculated radical chain-length distribution, $R(N)$ (dashed line), and dead chain-length distribution, $P(N)$ (solid line), for a styrene emulsion polymerization at 50 °C and $w_p = 0.5$ in which termination is solely by combination and independent of chain length and there is no transfer. Initiator concentration, [I], is $1 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$, $k_d$ is $1 \times 10^{-6}$ s$^{-1}$, swollen particle radius, $r_s$, is 150 nm, particle concentration, $N_c$, is $1 \times 10^{14}$ dm$^{-3}$, and the diffusion coefficient of all species, $D$, is $1.5 \times 10^{-10}$ cm$^2$ s$^{-1}$. The predicted value of $\bar{n}$ is 12.83.

The results for $R(N)$ and $P(N)$ are

$$R(N) = R(1) \exp\left[\frac{-2(k_t/N_A V_s)\bar{n}}{k_p[\mathrm{M}]}(N-1)\right] \quad (80)$$

$$P(N) = R(1)^2 \left(\frac{k_t}{N_A V_s}\right) \exp\left[\frac{-2(k_t/N_A V_s)\bar{n}}{k_p[\mathrm{M}]}(N-2)\right](N-2) \quad (81)$$

In eqs 80 and 81, $k_t = 4\pi\sigma D$, where $D$ is the chain-length-independent diffusion coefficient. In the derivation of eq 81 it is assumed that all termination is by combination rather than disproportionation. Transfer has not been included in this formulation because its inclusion would mean that there were two mechanisms for chain stopping which would complicate the forms of eqs 80 and 81. The form of these distributions under the conditions of a typical pseudobulk styrene emulsion polymerization can be seen in Figure 1. The maximum in $P(N)$ in Figure 1 occurs at $N = k_p[\mathrm{M}]N_A V_s / 2k_t\bar{n}$, and the magnitude of the slope of $R(N)$ is the inverse of this value, i.e., $2k_t\bar{n}/k_p[\mathrm{M}]N_A V_s$. A further point of interest is that the slope of $P(N)$ approaches the slope of $R(N)$ as $N$ approaches infinity. Phenomenologically, the maximum in $P(N)$ is due to the fact that as the degree of polymerization of polymer formed by termination increases there are more combinations of chain lengths that can combine to form any given length of dead polymer and that as chain length increases the population of radicals of that chain length decreases. Therefore, not many very short dead chains are formed because there are only a small number of combinations of chain lengths that can produce them, and not very many extremely long dead chains are produced because there are very few extremely long radicals.

The *number*-average molecular weight, $\langle M_n \rangle$, was 2.55 × 10$^6$ and the *weight*-average molecular weight, $\langle M_w \rangle$, was 3.83 × 10$^6$, giving a polydispersity, $\gamma$, of 1.5. A useful check of the computer code used to solve these equations is that the results from the coarse-grained method should be indistinguishable from those produced by using eqs 80 and 81. The data displayed in Figure 1 were produced using the coarse-grained and truncated

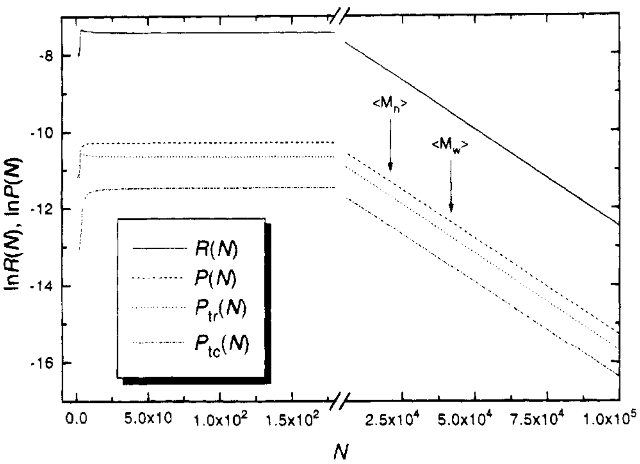

**Figure 2.** Calculated radical chain-length distribution, $R(N)$ (solid line), dead chain-length distribution, $P(N)$ (long-dashed line), dead chain-length distribution for chains killed by transfer, $P_{tr}(N)$ (dotted line), and dead chain-length distribution for chains killed by termination by combination, $P_{tc}(N)$ (dot–dashed line), for a styrene emulsion polymerization at 50 °C and $w_p = 0.5$ in which termination depends upon chain length and transfer to monomer is included. Conditions are identical to those of Figure 1 except that transfer and chain-length-dependent termination (solely by combination) have been included. The arrows indicate the positions of the *number*- and *weight*-average molecular weight distributions. The predicted value of $\bar{n}$ is 11.85.

methods discussed in section 5 and are indistinguishable from data produced by using eqs 80 and 81. As such Figure 1 and these equations act as a verification of our computer code.

**II. Chain-Length-Dependent Termination with Transfer.** We now turn our attention to a more realistic system in which we make allowance for the fact that microscopic termination rate coefficients depend upon chain length. This system is a styrene emulsion polymerization at $w_p = 0.5$ with an initiator concentration of $10^{-3}$ mol dm$^{-3}$, $k_d = 1 \times 10^{-6}$ s$^{-1}$, $p = 0.25$, and a particle concentration of $10^{14}$ dm$^{-3}$. The value of $\bar{n}$ determined for this system was 11.85, and the average termination rate coefficient was $2.82 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$. The value of $\langle M_n \rangle$ was $2.08 \times 10^6$, and that of $\langle M_w \rangle$ was $4.15 \times 10^6$, giving a polydispersity, $\gamma$, of 2.0. This value for the polydispersity is interesting because it was obtained in a system in which all termination occurs by a second-order process, i.e., combination. The reason for this behavior can best be seen by examining the form of the distributions of dead and living chains for this system.

Figure 2 shows the RCLD ($R(N)$) and CLD ($P(N)$) for this system as well as the contribution to the CLD due to transfer ($P_{tr}(N)$) and the contribution to the CLD due to termination by combination ($P_{tc}(N)$). The representation of distribution functions in Figure 2 and subsequent figures is designed to show a number of the features of the distribution in the same diagram. On the left-hand side of the axis break, the distribution at low degrees of polymerization is shown in an expanded manner so that the effect of chain-length-dependent rate parameters can be seen. The low molecular weight part of the distribution is also important due to the action of small species as plasticizers and their effect upon many physical properties. On the right-hand side of the axis break, the distribution at high degrees of polymerization is shown. From this part of the diagram it is easier to look at the absolute and relative magnitudes of the slopes of the distributions and to look at the relative amounts of polymer produced by each of the chain-stopping events. The positions of the two arrows indicate the positions of $\langle M_n \rangle$ and $\langle M_w \rangle$.

We shall firstly examine the form of $R(N)$ which is given approximately by eq 54. The qualification 'approximately' must be made here because the distribution $R(N)$ in Figure 2 includes the fact that entering species derived from initiator have a degree of polymerization $z$ whereas eq 54 was evaluated by assuming that such species are monomeric. The first notable fact about $R(N)$ is that it has a maximum which occurs at $N = z$, where $z = 3$ here. The concentrations of monomeric and dimeric radicals are lower than the concentration of trimeric radicals because the two former species can only be created by transfer while the latter species and all longer species can be created by both transfer and entry. As $N$ increases above $N = 3$, the concentration of each successive radical species decreases due to loss of radicals through termination and transfer. According to eq 58, the long-chain slope of ln $R(N)$ versus $N$, hereafter referred to as $m$, should be given by $-[k_{tr}/k_p + (\langle k_t \rangle \bar{n})/(k_p[\mathrm{M}]N_AV_s)]$ which has the value of $-5.046 \times 10^{-5}$ for this system. The slope of ln $R(N)$ at high $N$ from Figure 2 is $-5.053 \times 10^{-5}$, the small discrepancy in these two values being due to neglect of the small term due to reaction diffusion in going from eq 57 to 58. It should be noted here that the terms $k_{tr}/k_p = 3.49 \times 10^{-5}$ and $(\langle k_t \rangle \bar{n})/(k_p[\mathrm{M}]N_AV_s) = 1.56 \times 10^{-5}$ have values of the same order of magnitude, indicating that chain death is due to both transfer and combination in this system.

Figure 2 also contains the CLD, $P(N)$, and the two contributions to the CLD due to transfer, $P_{tr}(N)$, and combination, $P_{tc}(N)$. According to eq 60, $P_{tr}(N)$ should be proportional to $R(N)$, and Figure 2 shows this to be true. Perhaps surprisingly though, $P_{tc}(N)$ is also proportional to $R(N)$ for all but the smallest values of $N$. The explanation for this is not immediately obvious from the form of eq 60. The reason for this behavior is that the very shortest radicals have the highest termination probability due to their high diffusion coefficients and high concentrations, and so most termination events involve at least one radical which has a low degree of polymerization. Now, if we consider how long chains are terminated we observe that they are most likely to terminate with a short chain and to produce dead polymer that has a degree of polymerization only slightly longer than the longer of the radicals that was involved in the termination reaction. Consequently the distribution of long chains produced by termination by combination is similar to the distribution of radicals from which they are formed. However, for short chains the distribution $P_{tc}(N)$ is very different in form from $R(N)$. The important difference, a maximum in $P_{tc}(N)$ at about $N = 130$, has the same cause as the maximum in $P(N)$ in Figure 1, i.e., that there are relatively few combinations of radicals that can give short dead chains.

The final feature of Figure 2 that is worthy of comment is that in this system approximately the same number of dead chains are formed by transfer and combination. This is related to the fact that $k_{tr}/k_p$ and $(\langle k_t \rangle \bar{n})/(k_p[\mathrm{M}]N_AV_s)$ have approximately the same value.

**III. Effect of Changing the Critical Degree of Polymerization of Entering Species, *z*.** In section II account was taken of the fact that entering species derived from initiator are not monomeric but instead have a degree of polymerization $z$. In this section we examine how the RCLD and CLD depend upon the value of $z$. These distributions were evaluated for a system identical to that above except that in this case entering species derived from initiator were assumed

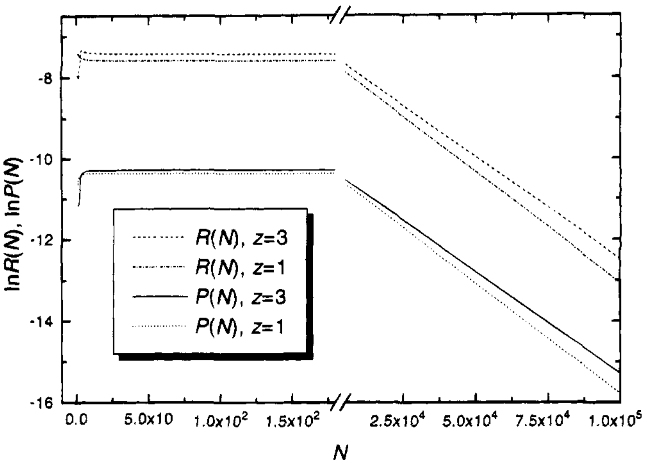

**Figure 3.** Comparison of the effect upon predicted $R(N)$ and $P(N)$ caused by varying the length of the entering species derived from initiator decomposition. The conditions are otherwise identical to those for Figure 2. Long-dashed line, $R(N)$ for $z = 3$; dot–dashed line, $R(N)$ for $z = 1$; solid line, $P(N)$ for $z = 3$; and dotted line, $P(N)$ for $z = 1$.

to be monomeric. The aim here is to evaluate the effect of changing the length of the entering radical. However, using a different value of $z$ will give a different value of $\varrho_I$ according to eq 77. For the purpose of this study, $\varrho_I$ was calculated as if $z = 3$ for both the case in which entering species were assumed to be trimeric and the case in which they were assumed to be monomeric. This was done to ensure that realistic values of $\varrho_I$ were obtained from eq 77 in both cases.

For the case in which entering species are monomeric, the value of $\bar{n}$ is 9.30 (compared to 11.85 for the case in which they are trimeric), $\langle k_t \rangle$ is $4.57 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$ (compared to $2.82 \times 10^4$), $\langle M_n \rangle$ is $1.92 \times 10^6$ (compared to $2.08 \times 10^6$), and $\langle M_w \rangle$ is $3.83 \times 10^6$ (compared to $4.15 \times 10^6$). From Figure 3 it can be seen that for the case in which $z = 1$ the populations of monomeric and dimeric radicals are much greater relative to all other populations than they are for the case in which $z = 3$. This results in increased termination and a decrease in $\bar{n}$. The decrease in the values of $\langle M_n \rangle$ and $\langle M_w \rangle$ is due to an increased value of $(\langle k_t \rangle \bar{n})/(k_p[\mathrm{M}]N_A V_s) = 1.98 \times 10^{-5}$ (compared to $1.56 \times 10^{-5}$ for the case where $z = 3$). Consequently, for the present case, approximately 36% of the dead polymer is created by termination by combination and only 64% by transfer.

The explanation for why changing $z$ from 3 to 1 has such an effect is that the average rate of termination depends strongly on the rate of termination of the smallest chains. Obviously, then, changing from the situation where there are relatively few monomeric and dimeric radicals to the situation where they are the most abundant species will have a significant effect upon the average termination rate and therefore upon the whole molecular weight distribution.

**IV. Effect of Varying $k_p$ for the First Propagation Steps.** There is a growing body of evidence[49–54] that suggests that the propagation rate coefficient, $k_p$, is larger for the first few propagation steps than it is once the chain becomes long. This work has already shown that the populations of the smallest radicals are important for the MWD and overall kinetics due to the high mobility of these species resulting in a high termination rate for these small species.

The magnitude of the ratio $k_p^1/k_p$ is not known with any certainty, but a value in the range of 5–10 is not thought to be unreasonable. Furthermore, if $k_p^1 = 10k_p$, then it should be expected that $k_p^2$ should also significantly exceed the long-chain propagation rate coefficient. Due to the lack of any concrete information about the values of $k_p^1$, $k_p^2$, etc., we here take values that seem reasonable to examine the effect that chain-length-dependent $k_p$ has upon the MWD and the parameters $\bar{n}$ and $\langle k_t \rangle$.

**Table 1. Comparison of Calculated $k_t$, $\bar{n}$, $\langle M_n \rangle$, and $\langle M_w \rangle$ for Various Values of $k_p^1$ and $k_p^2$**

| | $\langle k_t \rangle$ (dm$^3$ mol$^{-1}$ s$^{-1}$) | $\bar{n}$ | $\langle M_n \rangle$ | $\langle M_w \rangle$ |
|---|---|---|---|---|
| $k_p^1 = k_p^2 = k_p$ | $2.82 \times 10^4$ | 11.85 | $2.08 \times 10^6$ | $4.15 \times 10^6$ |
| $k_p^1 = 10k_p$, $k_p^2 = k_p$ | $2.00 \times 10^4$ | 14.10 | $2.18 \times 10^6$ | $4.36 \times 10^6$ |
| $k_p^1 = 10k_p$, $k_p^2 = 5k_p$ | $1.58 \times 10^4$ | 15.84 | $2.25 \times 10^6$ | $4.49 \times 10^6$ |

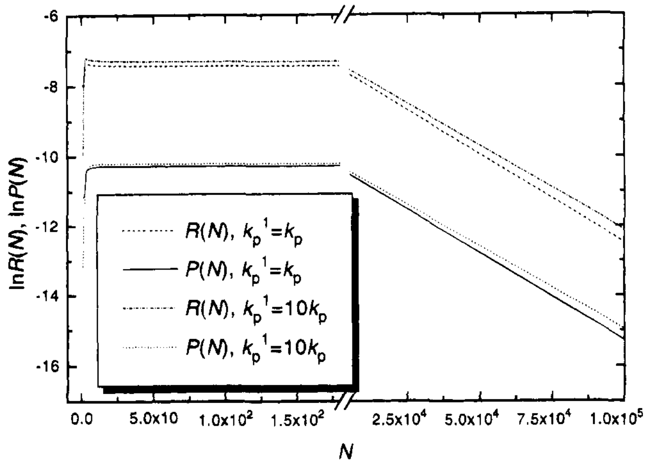

**Figure 4.** Comparison of the effect upon predicted $R(N)$ and $P(N)$ caused by varying $k_p^1$. The conditions are the same as those used for Figure 2. Long-dashed line, $R(N)$ for $k_p^1 = k_p$; dot–dashed line, $R(N)$ for $k_p^1 = 10k_p$; solid line, $P(N)$ for $k_p^1 = k_p$; and dotted line, $P(N)$ for $k_p^1 = 10k_p$.

Table 1 shows the results of calculations for the same system as that examined in section II above, as well as for the case in which $k_p^1 = 10k_p$, and the case in which $k_p^1 = 10k_p$ and $k_p^2 = 5k_p$. From Table 1 it can be seen that making the propagation rate coefficients for short chains larger than those for long chains decreases $\langle k_t \rangle$ and therefore increases $\bar{n}$. This result was also seen by Russell et al.[18] The product $\langle k_t \rangle \bar{n}$ also decreases resulting in larger values of $\langle M_n \rangle$ and $\langle M_w \rangle$. Figure 4 shows the RCLD, $R(N)$, and the CLD, $P(N)$, for the first and second of these cases. The reason for this behavior can easily be seen to be due to further decrease in the values of $R(1)$ and $R(2)$.

**V. MWD of Poly(methyl methacrylate) at Zero Conversion.** It is instructive to examine the predictions of our model for the MWD produced at zero conversion in bulk polymerizations because under such conditions it is easy to produce polymer over a small variation in weight fraction of polymer in the system. At higher conversions the molecular weight distribution measured will be a cumulative MWD over the whole polymerization, but by stopping polymerizations at only a few percent conversion it should be possible to measure what are essentially instantaneous MWDs.

The conditions employed for these simulations are those applicable to a methyl methacrylate polymerization at $w_p = 1 \times 10^{-4}$. The concentration of methyl methacrylate in this system was taken to be 9.39 mol dm$^{-3}$. The product $fk_d$ was taken to be $1.0 \times 10^{-6}$ s$^{-1}$ which is the value for AIBN at 50 °C, and a value of $p = 0.25$ was employed. For the variation of the center-of-mass diffusion coefficient of polymeric radicals, we employed a functional form based on eq 51 with a value

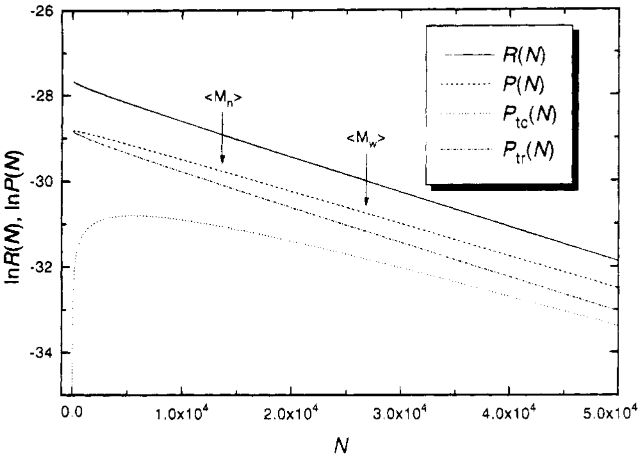

**Figure 5.** Predicted MWD and chain-length distribution of radicals for a methyl methacrylate bulk polymerization at $w_p = 1 \times 10^{-4}$ ("zero conversion"). Initiator concentration, [I], is $1.0 \times 10^{-3}$ mol dm$^{-3}$ and $fk_d$ is $1 \times 10^{-6}$ s$^{-1}$. Shown are (solid line) radical chain-length distribution, $R(N)$; (dashed line) dead chain-length distribution, $P(N)$; (dotted line) contribution to the CLD due to termination by combination, $P_{tc}(N)$; and (dot–dashed line) contribution to the CLD due to termination by transfer. The positions of the arrows indicate $\langle M_n \rangle$ and $\langle M_w \rangle$. The value of the radical concentration is $1.06 \times 10^{-8}$ mol dm$^{-3}$.

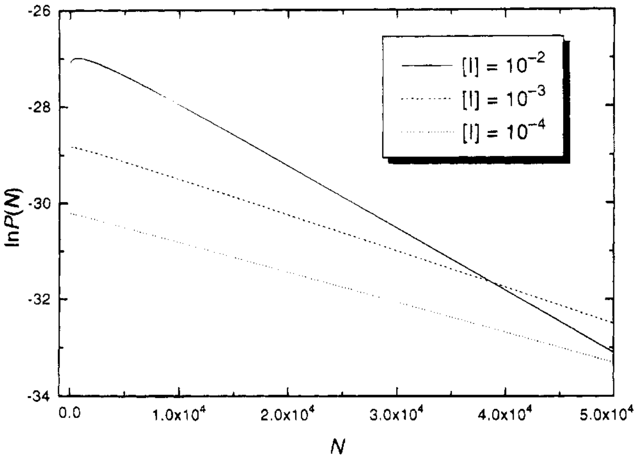

**Figure 6.** Molecular weight distribution of polymer predicted at "zero conversion" as a function of initiator concentration. Solid line, [I] = $1.0 \times 10^{-2}$ mol dm$^{-3}$; dashed line, [I] = $1.0 \times 10^{-3}$ mol dm$^{-3}$; and dotted line, [I] = $1.0 \times 10^{-4}$ mol dm$^{-3}$. All other conditions are identical to those of Figure 5. All termination is by combination.

of $\alpha = 0.5$ for all $N$. We realize that this dependence of diffusion coefficient upon chain length is probably not physically correct for long chains. However, as has already been seen for systems in which microscopic termination rates are dependent upon chain length, it is the termination events involving the shortest chains which govern the molecular weight distribution, and therefore the variation employed here for long chains should not greatly affect the form of the MWD predicted.

Figure 5 shows the predicted RCLD, $R(N)$, and the CLD, $P(N)$, as well as the contributions to the CLD from combination, $P_{tc}(N)$, and transfer, $P_{tr}(N)$, for a zero conversion methyl methacrylate polymerization in which the initiator concentration, [I], is $1.0 \times 10^{-3}$ mol dm$^{-3}$. The predicted average termination rate coefficient is $9.1 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$. The arrows in Figure 5 indicate the positions of $\langle M_n \rangle$ at a molecular weight of $1.35 \times 10^6$ and $\langle M_w \rangle$ at a molecular weight of $2.67 \times 10^6$, giving a polydispersity of 1.98. Even though the polydispersity of this polymer is close to 2.0, the effect of the weaker dependence of the termination rate upon chain length can be seen in the form of the contribution to the CLD due to combination, which has a maximum at a molecular weight of $5.55 \times 10^5$, due to the reduced proportion of very small radicals evident in the form of $R(N)$.

In performing these simulations it was assumed that termination by disproportionation does not occur. If the situation were to exist in which all termination was by disproportionation, then the MWD of chains produced by disproportionation would have no maximum. Figure 6 shows the MWDs predicted under the same conditions as for Figure 5, i.e., all termination by combination, except that initiator concentration has been varied over the range from $1.0 \times 10^{-2}$ to $1.0 \times 10^{-4}$ mol dm$^{-3}$. It can be seen that as initiator concentration increases the average molecular weight of the polymer decreases and that for the highest initiator concentration there is a distinct maximum in the plot of ln $P(N)$ at a molecular weight of $6.7 \times 10^4$. The MWD under equivalent conditions, except that all termination is by disproportionation, would have *no* maximum. Therefore, the measurement of MWDs at "zero conversion" can provide evidence, although by no means definitive, as to the type of termination that occurs in these systems. Significant deviation from the predictions of this work could be attributed to segmental diffusion.

Of further mechanistic interest is the fact that as the initiator concentration is reduced at zero conversion the slope of ln $P(N)$ at large $N$ approaches the limiting value of $-(k_{tr}/k_p)$. If combined with values of $k_p$ determined by pulsed laser polymerization,[55,56] then this provides a method of determining the rate coefficient for transfer to monomer. Such a technique can also be trivially extended to enable to the measurement of transfer rate coefficients to added chain-transfer agents.[57]

**VI. Measuring Transfer Constants from MWDs.** From the form of eq 59 it is apparent that if, in an emulsion system, the term $\langle k_t \rangle \bar{n}/k_p[\mathrm{M}]N_A V_s$ is small compared to the transfer constant, $k_{tr}/k_p$, then one could measure the transfer constant from a plot of ln $R(N)$ versus $N$. However, it is not possible to measure the chain-length distribution of radicals (living chains) but only the distribution of dead chains. Fortunately, as shown in section II above, for large values of $N$ the slope of a plot of ln $R(N)$ versus $N$ and the slope of a plot of ln $P(N)$ versus $N$ are identical.

The easiest method of reducing the size of the term $\langle k_t \rangle \bar{n}/k_p[\mathrm{M}]N_A V_s$ is to reduce the initiator concentration in the system. Figure 7 shows $P(N)$ predicted for a styrene emulsion polymerization at 50 °C, $w_p = 0.7$, a swollen particle radius of 150 nm, and $N_c = 1 \times 10^{14}$ dm$^{-3}$, as a function of initiator concentration. The value of $k_d$ used was $1 \times 10^{-6}$ s$^{-1}$. As the initiator concentration is reduced, the magnitude of the slope (at large $N$) of a ln $P(N)$ versus $N$ plot becomes smaller, approaching the limiting value of $-k_{tr}/k_p$ (indicated by the solid line). The initiator concentrations used in these simulations were $1 \times 10^{-3}$, $1 \times 10^{-4}$, and $1 \times 10^{-5}$ mol dm$^{-3}$ (indicated by the dashed, dot–dashed, and dotted lines, respectively). The predicted values of $\bar{n}$ were 11.85, 8.60, and 4.60, respectively. The magnitude of the slope of the plot for an initiator concentration of $1 \times 10^{-5}$ mol dm$^{-3}$ was $4.05 \times 10^{-5}$, only 16% greater than the value of $k_{tr}/k_p$. This shows that reasonable estimates of $k_{tr}/k_p$ can be obtained if it is possible to measure instantaneous MWDs, particularly as a function of initiator concentration.

Although only the time-cumulative MWD is available from experiment, it still may be possible to extract

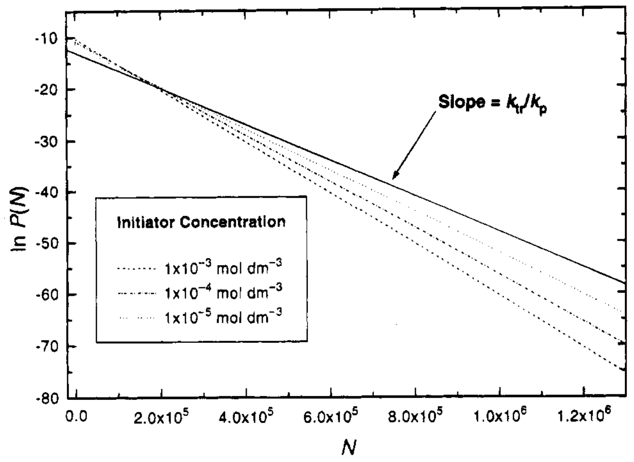

**Figure 7.** Predicted MWD of polymer produced for a styrene polymerization at 50 °C, $w_p = 0.7$, and $r_s = 150$ nm as a function of initiator concentration with $k_d = 1 \times 10^{-6}$ s$^{-1}$. The initiator concentrations are $1 \times 10^{-3}$ mol dm$^{-3}$ (dashed line), $1 \times 10^{-4}$ mol dm$^{-3}$ (dot–dashed line), and $1 \times 10^{-5}$ mol dm$^{-3}$ (dotted line). The solid line has a slope of $-k_{tr}/k_p$, which is the slope of the predicted MWD for an initiator concentration of zero.

values for the transfer constant from such data. It must be realized that during the course of a polymerization the longest polymer will be produced when $\langle k_t\rangle\bar{n}/k_p[\mathrm{M}]N_AV_s$ is at a minimum. Consequently, if one measures the slope of a ln $\hat{P}(N)$ versus $N$ plot in the limit as $N$ approaches infinity, then the polymer chains being examined are those produced when $\langle k_t\rangle\bar{n}/k_p[\mathrm{M}]N_AV_s$ is at a minimum. The value of this slope will then give an upper bound to the transfer constant, $k_{tr}/k_p$. If these upper bounds to the transfer constant are measured as a function of initiator concentration, then the values can be extrapolated to zero initiator concentration to provide an estimate of $k_{tr}/k_p$.

The value of $k_{tr}/k_p$ has been measured by a similar technique, i.e., plotting ln $P(N)$ versus $N$ and measuring the slope at large $N$, by Whang et al.[28] in zero–one emulsion polymerizations for methyl methacrylate and styrene. More recently, Heuts et al.[57] have measured $k_{tr,A}$ and $k_{tr,M}$ (the rate coefficients for transfer to chain-transfer agent and transfer to monomer) by a related technique for a bulk triethylamine/methyl methacrylate system at low conversion.

## 7. Obtaining the Number MWD from Size Exclusion Chromatography (SEC)

The predictions about MWDs made in this work would be little more than arcana if no method existed for their measurement. The technique of choice for this purpose is size exclusion chromatography (also known as gel permeation chromatography). We here provide the theoretical development of a technique for obtaining the number MWD, $\hat{P}(M)$, from a size exclusion chromatograph. Note that SEC can only directly measure the MWD of all the polymer in the system at a particular time and not the instantaneous MWD, $P(M)$. To determine instantaneous MWDs, one must measure the evolution of the MWD in time and then differentiate with respect to time.

The quantity most often measured by detectors in SEC (differential refractive index and UV absorption) is the (relative) concentration of polymer as a function of the volume of solvent eluted from the system. We give this the symbol $G(V_{el})$ where $V_{el}$ is the elution volume. Now because of the nature of the chromatographic system, the polymer chains passing the detector at any time would normally span a range of molecular weights. Therefore the detector signal at a particular elution volume is comprised of a sum of signals from different molecular weights. We write[28]

$$G(V_{el}) = \int_0^\infty K(V_{el},M)\hat{P}(M)\mathrm{d}M \equiv \int_0^\infty R(V_{el},M)W(M)\mathrm{d}M \tag{82}$$

where $R(V_{el},M) = K(V_{el},M)/M$ is the apparatus response function which depends upon the SEC system. Therefore, in order to obtain $\hat{P}(M)$, one must deconvolute $G(V_{el})$.

To effect deconvolution of $G(V_{el})$, one must know the relationship between elution volume and molecular weight for the system under consideration. To determine this relationship, polymer standards (assumed here to be of the same composition as the samples to be analyzed) with low polydispersities and known peak molecular weights are passed through the SEC system. From this one obtains a "calibration curve", $\mathcal{V}(M)$. We suppose that a monodisperse standard, i.e., one where $W(M) = \delta(M - M')$, gives a very narrow response, i.e., $G(V_{el}) = A(M')\delta[V_{el} - \mathcal{V}(M)]$, where $A(M')$ is a normalization function. The function $A(M')$ can be found by noting that the detector response, $G(V_{el})$, is proportional to the total mass of polymer passing the detector. The total mass for a (nearly) monodisperse standard can be expressed in terms of the weight MWD, $W(M)$, as an integral:

$$\text{total mass} = \int_{M'-\epsilon}^{M'+\epsilon} W(M)\mathrm{d}M = \int_{M'-\epsilon}^{M'+\epsilon} \delta(M - M')\mathrm{d}M = 1 \tag{83}$$

We have here assumed unit mass of sample. The signal intensity is similarly the integral of $G(V_{el})$ over the narrow elution volume range of the standard.

$$\text{detector response} = \int_{\mathcal{V}(M')-\epsilon}^{\mathcal{V}(M')+\epsilon} G(V_{el})\mathrm{d}V_{el} = \int_{\mathcal{V}(M')-\epsilon}^{\mathcal{V}(M')+\epsilon} A(M')\delta[V_{el} - \mathcal{V}(M')]\mathrm{d}V_{el} = A(M') \tag{84}$$

From eqs 83 and 84, and by noting that detector response is always proportional to total mass, one can state that $A(M')$ is independent of molecular weight, and for simplicity it is henceforth given the value of unity.

We can now identify the quantity $R(V_{el},M)$ of eq 82:

$$\delta[V_{el} - \mathcal{V}(M')] = \int_0^\infty R(V_{el},M)\delta(M - M')\mathrm{d}M = R(V_{el},M') \tag{85}$$

Therefore

$$R(V_{el},M') = \delta[V_{el} - \mathcal{V}(M')] \tag{86}$$

which gives

$$G(V_{el}) = \int_0^\infty \delta[V_{el} - \mathcal{V}(M)]W(M)\mathrm{d}M \tag{87}$$

To perform the integration of eq 89, we employ the definition of a $\delta$ function

$$\int_0^\infty f(x)\mathrm{d}(x - a)\mathrm{d}x = f(a) \tag{88}$$

and change variables from $M$ to $\mathcal{V}$. Equation 89 then becomes

$$G(V_{\mathrm{el}}) = \int_0^\infty \delta(V_{\mathrm{el}} - \mathcal{V}) W(M(\mathcal{V})) \frac{\mathrm{d}M}{\mathrm{d}\mathcal{V}} \mathrm{d}\mathcal{V} = W(M(\mathcal{V})) \frac{\mathrm{d}M}{\mathrm{d}\mathcal{V}} = M\hat{P}(M(\mathcal{V})) \frac{\mathrm{d}M}{\mathrm{d}\mathcal{V}} \quad (89)$$

Rearranging eq 89 gives an expression for $\hat{P}(M)$:

$$\hat{P}(M(\mathcal{V})) = \frac{G(V_{\mathrm{el}})\,\mathrm{d}\mathcal{V}}{M \quad \mathrm{d}M} \quad (90)$$

It is common for the calibration curve, $\mathcal{V}(M)$, to be represented as a relationship between $\log_{10} M$ and a low order polynomial in elution volume. For some SEC columns, the calibration curve is log-linear, i.e., $\log_{10} M = a + b\,\mathcal{V}(M)$, over a large range of molecular weights and hence $\mathrm{d}M/\mathrm{d}\mathcal{V} \propto M$, giving (for the linear region of the calibration curve):

$$\hat{P}(M) = (\text{arbitrary constant}) \times \frac{G(V_{\mathrm{el}})}{M^2} = (\text{arbitrary constant}) \times \frac{W(M)}{M} \quad (91)$$

This result and the above treatment give the same results, though with a different formalism, as the recent work of Shortt[58] in this area. The factor of $M^2$ occurs in eq 91 because (1) the SEC detector signal is proportional to the mass of polymer passing the detector, giving a factor of $M$, and (2) the log-linear calibration curve means that a volume increment, $\mathrm{d}\mathcal{V}$, is proportional to $\mathrm{d}M/M$, giving another factor of $M$. Equation 91 corrects an error contained in the work of Morrison et al.[59] and eq 2 of Whang et al.[28]

## 8. Discussion and Conclusions

Modeling of the molecular weight distribution in free-radical polymerizations requires a detailed knowledge of all the kinetic events that occur during the creation of that polymer. This work presents derivations of the MWD expected for systems in which the kinetics are thought to be well-understood, and for the case of systems in which pseudobulk kinetics apply, a method of numerically solving the equations defining the MWD has been developed. The effects of changing various parameters of pseudobulk systems were then examined, and it was found that the kinetics and the molecular weight distribution are sensitive to the rate coefficients for the very shortest chains. This result is a direct consequence of the inclusion of chain-length-dependent termination rate coefficients in our kinetic scheme.

We have developed here equations which describe the complete molecular weight distribution in any free-radical polymerization in which branching and cross-linking are unimportant. Methods are also described which enable numerical solutions to be obtained for the nonlinear integrodifferential equations which specify the MWD. The scheme takes into account initiation, transfer, propagation, and termination, allowing all of these to be dependent upon the degrees of polymerization of the growing chains involved. The model is applicable to bulk and solution polymerizations and to compartmentalized systems (conventional and micro- and mini-emulsion polymerizations); in the latter case, phase-transfer events (radical entry into and exit from latex particles, and the aqueous phase kinetics of the various radical species) are specifically included. The dependence of the termination rate coefficient upon the lengths of both participating chains is especially important in systems where termination is kinetically significant.

Our techniques also given approximate analytic solutions to the MWD equations in certain limiting cases which are nevertheless acceptable descriptions for many systems of interest. These show that the intantaneous number MWD for higher molecular weights is a single exponential in emulsion polymerizations with a low number of radicals per particle; moreover, in many cases, this instantaneous MWD will be independent of conversion, and hence the exponential behavior for higher molecular weights will also be apparent in the cumulative MWD. Importantly, in many systems where termination is kinetically dominant, a single-exponential behavior in the instantaneous MWD is also predicted; this is because longer living chains cease growth either by transfer or by termination, and the terminating chain is likely to be a mobile short free radical. Moreover, the cumulative MWD frequently has the same behavior as the instantaneous MWD. This shows that chain-transfer constants can be measured experimentally by examining the high molecular weight part of the number MWD, including its behavior as initiator concentration is varied; this enables chain-transfer constants to be measured even in systems where termination is extensive.[57] In addition, observed deviations from exponential behavior should enable mechanistic deductions to be made about chain-stopping events.[28,59]

Approximate analytical solutions have been developed for a number of cases of interest. This has the important implication that considerable mechanistic information can be obtained from size exclusion chromatography data by plotting the log(number MWD) against molecular weight. Illustrative calculations have been carried out for a number of systems. These verify the conclusions from the approximate analytic solutions and show also that the MWD in bulk or solution polymerizations at low conversions should show a low molecular weight maximum at high initiator concentrations.

We have shown here that the number MWD is a sensitive indicator of a number of mechanistic events in free-radical polymerizations, and hence an experimental MWD can yield considerable mechanistic information. The cumulative number MWD is easily obtained experimentally from SEC. The instantaneous MWD can be obtained in principle from a succession of SEC results taken as a function of conversion; moreover, our theoretical treatment shows that in many cases part of the cumulative MWD (the cumulative MWD of long chains) is the same as the instantaneous MWD over a large conversion range. Hence there is the potential for obtaining considerable information on chain-stopping and -starting events, as well as control over many important technical properties, from SEC data with little additional effort beyond that needed to measure $\langle M_{\mathrm{w}}\rangle$ and $\langle M_{\mathrm{n}}\rangle$. Furthermore, a similar technique can be used to estimate transfer constants. The theoretical and numerical techniques in this paper indicate how such information can be obtained.

While the results of this paper are interesting and allow one to understand the features of the kinetic scheme presented herein, it is important that they be compared to both kinetic data and molecular weight distributions obtained from experiments. We have presented a rigorous method for deriving the number MWD from size exclusion chromatography data, which will allow the predictions made in this work to be tested.

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