Chain-Length-Dependent Termination Rate Processes in Free-Radical Polymerizations. 1. Theory

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ABSTRACT: A complete set of rate equations describing the kinetics of free-radical polymerization is deduced, in which termination rate coefficients are allowed to depend on chain length. The rate equations are applicable to bulk, solution, and heterogeneous (e.g., emulsion) polymerization systems. They incorporate the following kinetic processes: initiation, propagation, transfer, chain-length-dependent termination, and, for emulsion systems, exit and reentry (i.e., aqueous-phase kinetic processes are taken into account). It is shown that, despite their apparent complexity, the full set of population balance equations can, to a good approximation, be reduced to a single first-order differential equation. This equation and that for the overall rate of polymerization form a pair of coupled differential equations that can be solved easily and are thus suitable for routine modeling of experiment. The key parameters required in the model are the rate coefficients for transfer and propagation and the diffusion coefficient of the monomer as a function of the polymer weight fraction (conversion), this variation being used in expressions for the dependence of the termination rate coefficient on the length of a growing chain. In accord with previous experiment and theory (Adams, M. E.; Russell, G. T.; Casey, B. S.; Napper, D. H.; Gilbert, R. G.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624), the present theory indicates that, at intermediate conversions, termination is dominated by interactions between short chains formed by transfer and entangled long chains. In the regime in which propagation is diffusion-controlled, most termination events involve two highly entangled chains, whose ends move by the "reaction-diffusion" process (Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2133). The mathematical treatments of this paper are of very general applicability and should inter alia be useful in addressing practical problems such as minimizing the residual monomer content of polymer products.

1. Introduction

As monomer is converted into polymer, the viscoelastic properties of a polymerizing system change enormously. These changes will not affect the rates of "chemically-controlled" reactions such as transfer and (except at high conversions) propagation (by "chemically-controlled" we mean that the rate-determining reaction step is that of passing through an enthalpic and/or entropic barrier at the transition state for the reaction between two moieties in close proximity). However, changes in viscoelastic properties must have a strong influence on those kinetic events that are diffusion-controlled. It has long been realized that termination interactions in free-radical polymerizations are in the latter category. This realization begs the following question: what is the diffusion mechanism which determines the rate of free-radical annihilation? Here again several ideas are well established. At low conversions it is usual to distinguish two diffusion steps in the termination process. In the first place, center-of-mass diffusion must render two macroradicals proximate. Once this has occurred, the two chain ends must encounter each other, this taking place by "segmental diffusion" (by which is meant the diffusion consequent upon reorientational chain backbone motions of a macroradical). Largely on account of the classic work of Benson and North in 1962,[1] these concepts are well-known. Not quite so widely known is the suggestion by Schulz from 1956[2] that at high conversions termination may occur by "reaction-diffusion" (also termed "residual" termination[3]). In this picture, termination occurs as a result of the propagation-induced diffusion of the chain end of a growing macroradical. It has recently been shown[4] that this concept may be used to rationalize much high-conversion kinetic data. Any accurate model of polymerization not only must include these different mechanisms of termination but also must allow the dominant termination mechanism to change with conversion.

A second major consequence of termination being diffusion-controlled is that a termination rate coefficient (k_t) must depend on the lengths of the growing chains undergoing termination. This is because, in general, rates of (center-of-mass) diffusion of polymeric species vary dramatically with their degree of polymerization, especially when any significant quantity of polymer is present. That termination rate coefficients might depend on chain length was clearly recognized and allowed for by Benson and North[1] (indeed, in this seminal paper can essentially be found some of the basic polymerization equations of the present work). Despite this, the actual application of this idea to the modeling of polymerization data is not all that common; Cardenas and O'Driscoll[5,6] have been pioneers in this respect.

For these two reasons, the development of an all-encompassing "microscopic" description of the termination process in free-radical polymerization would seem to be an exceedingly complex task. Moreover, it might appear that the resulting equations would contain so many adjustable parameters that a proper testing of the model against experiment (including opportunities for refutation[7]) would be impossible: with so many adjustable parameters, it would appear that accord with data could always be obtained and hence that such modeling would be no more than an exercise in curve-fitting, with no gain in knowledge or understanding.

Despite this consideration, many workers have opted to take the above approach. Amongst such are Cardenas and O'Driscoll,[5,6] Tulig and Tirrell,[8] Soh and Sundberg,[9] Olaj and co-workers,[10] Bamford,[11] and Mahabadi.[12,13] The first three of these groups set down kinetic equations for each individual chain length of free-radical species. The first two groups then attempted to simplify these equations to a more compact form involving various average radical concentrations only. Soh and Sundberg[9] did likewise but deduced a more advanced treatment wherein an overall k_t was obtained by appropriate averaging of the chain-length-dependent k_t held to be appropriate. Through modeling of experimental data, three groups[5,6,8,9] sought

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to evaluate the accuracy of their models of termination. Olaj and co-workers[10] allowed termination to be completely chain-length dependent and assumed that the appropriate k_t's were the geometric means of the chain lengths of the species involved. Against this approach, it must be pointed out that, if termination is diffusion-controlled, then according to the Smoluchowski equation k_t is proportional to the mutual diffusion coefficient of the two chains involved and so is not a simple function of any mean radical size. This criticism can also be leveled at the work of Bamford.[11] Lastly, Mahabadi[12,13] assumed that termination rate coefficients depend only on a power of the product ij of the chain lengths i and j of the two terminating species; there does not seem to be any general physical justification for such an assumption. In all of the work just cited, some approximations were made in order to reduce the chain-length-dependent equations, of varying degrees of completeness, to more tractable forms. In each case this was done without comparison to exact numerical solutions of the full equations, and so the accuracy of these approximations went unchecked.

Yet another way of handling chain-length-dependent termination has been that of our own group,[14] which by categorizing chains as either "long" or "short" adopted an Occam's-razor approach to this problem. However, such a categorization, while enabling experimental data to be readily interpreted by virtue of the mathematical simplicity of the equations so resulting, poses the problem of a precise definition of the boundary between short and long species and paints with too broad a brush to enable fine details (and hence perhaps inappropriateness of the model) to be adequately tested.

It is therefore the objective of the present paper to develop a full and stringently tested microscopic depiction of termination. Moreover, by taking as often as possible a perspective which is molecular, we deduce equations which contain only precise physical quantities, as few as possible of which are adjustable parameters. Further, we deduce approximations to these complete equations which are sufficiently easy to solve so as to be able to be routinely compared with experiment and which have also been tested against exact numerical solutions of the complete equations.

The present paper will be seen to provide a routine tool for testing and predicting rates in bulk and heterogeneous free-radical polymerizations. Being heterogeneous, a greater range of kinetic events occurs in emulsion systems than in bulk systems. In bulk systems, the initiator efficiency may be a sensitive function of conversion at intermediate and high conversions.[15] Since little is known about this variation, it is essentially impossible to use intermediate- and high-conversion bulk polymerization data as a probe of the accuracy of models of termination. On the other hand, no such variation is thought to occur in emulsion systems, which are therefore better suited to testing the rectitude of different models for termination. The advent[14,16] of extensive γ-radiolysis relaxation data for carefully characterized and controlled emulsion polymerization systems, wherein free-radical loss is dominated by termination, has provided the wherewithal to test the resulting descriptions in a definitive way against intermediate- and high-conversion experimental data. It is most important to note that these relaxation data provide information which is qualitatively different from, and complementary to, conversion–time curves from simple chemically initiated experiments, these latter having hitherto provided the only means of making such tests. Therefore in the present paper not only is a molecular-level description of the termination process provided but also computationally tractable means of critically evaluating this model against sensitive experimental data are deduced. The fitting of extensive γ-relaxation data of styrene and methyl methacrylate emulsion polymerizations has been carried out[17] and will be detailed in a subsequent publication.[18]

2. Formulation of Complete Equations

The model we present here is applicable to any type of free-radical polymerization: bulk, solution, suspension, or emulsion. Kinetic equations for bulk and solution polymerizations are best expressed in terms of the concentration of free radicals, $[\mathrm{R}^\bullet]$; the kinetics of emulsion polymerizations are best expressed in terms of the average number of free radicals per latex particle, $\bar{n}$. Our equations in the present paper will therefore be given in two forms: in $\bar{n}$ (ones where the equation number is "a") for emulsion (heterogeneous) systems and in terms of $[\mathrm{R}^\bullet]$ (ones in which the equation number is "b") for bulk and solution systems. The relationship for interconversion is

$$\bar{n} = [\mathrm{R}^\bullet] N_\mathrm{A} V_\mathrm{s} \tag{1}$$

Here N_A is Avogadro's constant and V_s the swollen volume of a latex particle.

In emulsion polymerization systems, free radicals are compartmentalized, and so strictly speaking the kinetics of such systems should be treated in terms of the discrete populations[19] $N_n(t)$ of latex particles containing n free radicals ($n = 0, 1, 2, ...$) at time t. However, we here adopt the so-called "pseudobulk" approximation:[20] as stated, we consider $\bar{n}(t)$, a single time-dependent variable, rather than the discrete $N_n(t)$. This approximation is quite justified under the present circumstances, because we are interested in systems wherein termination is rate-determining. For an emulsion polymerization system, this pseudobulk approximation has been proved[16,20] to give an excellent approximation to the true (discrete population) kinetics (i.e., compartmentalization effects can be safely ignored) when $\bar{n}$ is comparatively large (significantly greater than 0.5) and under certain conditions (e.g., when all desorbed free radicals undergo reentry) also to be quantitatively accurate when $\bar{n}$ is on the order of and even less than 0.5.

In the simplest treatment of pseudobulk emulsion polymerization kinetics, one has the following equation for the time evolution of the concentration of free radicals:[16,20]

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho - k\bar{n} - 2c\bar{n}^2 \tag{2a}$$

The analogous equation for a bulk system is

$$\mathrm{d}[\mathrm{R}^\bullet]/\mathrm{d}t = 2k_\mathrm{d}f[\mathrm{I}] - 2\langle k_\mathrm{t}\rangle[\mathrm{R}^\bullet]^2 \tag{2b}$$

In these equations ρ is the pseudo-first-order rate coefficient for entry of all free radicals into the latex particles, k is the rate coefficient for exit (desorption) of free radicals from the latex particles, $\langle k_\mathrm{t}\rangle$ is the (overall) (second-order) termination rate coefficient, $c = \langle k_\mathrm{t}\rangle/(N_\mathrm{A}V_\mathrm{s})$ is the pseudo-first-order rate coefficient for termination within a latex particle (c is the rate of termination per particle per free radical), k_d is the initiator decomposition rate coefficient, f is the initiator efficiency, and [I] is the initiator concentration. Note that we denote the termination rate coefficient in such equations as the average quantity $\langle k_\mathrm{t}\rangle$, since these equations take no account of the chain-length dependence of the termination rate coefficient; this deficiency will be redressed by the equations developed later in this paper.

Our objective is to write down much more complete equations that take into account the dependence of the various kinetic events on chain length. To this end, we define the concentrations T_i of growing chains of degree of polymerization i. The normalization of these populations is defined to be, for the emulsion and bulk cases, respectively

$$\sum_{i=1}^{\infty} T_i = \bar{n} \tag{3a}$$

$$\sum_{i=1}^{\infty} T_i = [\mathrm{R}^{\bullet}] \tag{3b}$$

In the emulsion system case, T_i is thus the average number of free radicals of degree of polymerization i per latex particle, while for bulk systems $T_i = [\mathrm{R}^{\bullet}{}_i]$, the actual concentration of i-meric free radicals in the system.

To deduce the evolution equations for the T_i, we consider the following kinetic events, in addition to those specified in eq 2 above: propagation, by which an i-mer grows to an $(i + 1)$-mer, with rate coefficient k_p; transfer, by which any i-mer becomes a monomeric free radical, with rate coefficient k_{tr} (for notational simplicity, we only consider transfer to monomer, the extension of the resulting equations to include added chain-transfer agent being straightforward; the present treatment ignores the case of transfer to polymer); for the case of emulsion polymerizations, it is assumed that exit is restricted to monomeric ($i = 1$) free radicals, these being formed by transfer and having a probability β of desorbing. Reentry of these species can be taken into account via the so-called "fate parameter" α,[21] which is a dimensionless quantity whose value must lie in the range $-1 \leq \alpha \leq 1$; the reentry contribution to the first-order entry rate coefficient is then[22,23] $\alpha k \bar{n} = \alpha\beta k_{tr}[\mathrm{M}]\bar{n}$, where [M] is the monomer concentration. This treatment of exit and reentry follows from the transfer/diffusion mechanism for exit of Ugelstad, Hansen, and Nomura,[22,23] a model which has been shown[24] to be in good accord with experiment.

Given all the kinetic events outlined above, the evolution equations for the T_i can be written as follows:

$$\frac{\mathrm{d}T_1}{\mathrm{d}t} = \rho_A + k_{tr}[\mathrm{M}]\sum_{i=2}^{\infty} T_i - k_p{}^1[\mathrm{M}]T_1 - \beta k_{tr}[\mathrm{M}]\sum_{i=2}^{\infty} T_i + \alpha\beta k_{tr}[\mathrm{M}]\sum_{i=2}^{\infty} T_i - 2T_1\sum_{i=1}^{\infty} c_{1i}T_i \tag{4a}$$

$$\frac{\mathrm{d}T_1}{\mathrm{d}t} = 2k_d f[\mathrm{I}] + k_{tr}[\mathrm{M}]\sum_{i=2}^{\infty} T_i - k_p{}^1[\mathrm{M}]T_1 - 2T_1\sum_{i=1}^{\infty} k_t{}^{1i}T_i \tag{4b}$$

$$\frac{\mathrm{d}T_2}{\mathrm{d}t} = -k_{tr}[\mathrm{M}]T_2 + k_p{}^1[\mathrm{M}]T_1 - k_p[\mathrm{M}]T_2 - 2T_2\sum_{i=1}^{\infty} c_{2i}T_i \tag{5a}$$

$$\frac{\mathrm{d}T_2}{\mathrm{d}t} = -k_{tr}[\mathrm{M}]T_2 + k_p{}^1[\mathrm{M}]T_1 - k_p[\mathrm{M}]T_2 - 2T_2\sum_{i=1}^{\infty} k_t{}^{2i}T_i \tag{5b}$$

$$\frac{\mathrm{d}T_i}{\mathrm{d}t} = -k_{tr}[\mathrm{M}]T_i + k_p[\mathrm{M}](T_{i-1} - T_i) - 2T_i\sum_{j=1}^{\infty} c_{ji}T_j, \quad i > 2 \tag{6a}$$

$$\frac{\mathrm{d}T_i}{\mathrm{d}t} = -k_{tr}[\mathrm{M}]T_i + k_p[\mathrm{M}](T_{i-1} - T_i) - 2T_i\sum_{j=1}^{\infty} k_t{}^{ji}T_j, \quad i > 2 \tag{6b}$$

Here [M] is the monomer concentration in the locus of polymerization, ρ_A is the component[21] of the overall entry rate coefficient arising directly from the aqueous-phase initiator (plus any background thermal component), and f is the initiator efficiency (for the case of bulk/solution systems). Some points in explanation of the above equations are as follows:

(a) Free radicals are distinguished solely according to the number of monomer units they contain; i.e., no distinction is made between initiator-derived free radicals and transfer-generated free radicals. Of course, different sets of population balance equations could be written down for these two free-radical types. However, this has not been done, first for simplicity and second because it is not really necessary: except if i is very small, the behavior (and in particular the rate at which it terminates) of an i-meric free radical is not really dependent on whether it was born by transfer or initiator decomposition.

(b) In eq 4a it has been assumed (for the case of emulsion polymerizations) that entry (of initiator-derived free radicals) and reentry (of desorbed free radicals) are of monomeric species only. Entering species may in fact[25] be dimeric, trimeric, or of an even slightly greater degree of polymerization, but an exact numerical solution of the above equations shows that changing the degree of polymerization of the entering species over such a range has no effect on the overall kinetics.[17,18] This is because the above scheme (correctly) does not allow entering species to exit, and propagation of entering free radicals occurs quickly on the time scale of competing kinetic events. Note, however, that, as has been implied, the above equations are easily adjusted to allow entry and reentry of other than monomeric free radicals.

(c) We have allowed for the possibility that the rate coefficient for propagation of a monomeric free radical, denoted $k_p{}^1$, may be different from that for propagation of free radicals of higher degree of polymerization. Again, the above equations are trivially altered to allow further chain-length dependence of propagation.

(d) In equations for heterogeneous systems, rate coefficients for termination between chains of length i and j are written in a pseudo-first-order form

$$c_{ij} = k_t{}^{ij}/N_A V_s \tag{7}$$

where $k_t{}^{ij}$ is the corresponding chain-length-dependent second-order rate coefficient for termination. Note also that termination rate coefficients have been defined so that all termination interactions result in the loss of two free radicals of the type whose rate equation is being written down.

Equations 4–6 are population balance equations and (except for the terms involving the emulsion-specific events of entry and reentry) contain essentially no assumptions as to mechanism. It is useful at this point to generate some numerical solutions, with a view to obtaining information that can be used to make physically acceptable simplifications to eqs 4–6. For these sample calculations, we must obviously make some model-based assumptions in order to specify values of all parameters. The separate issue of the accuracy of these assumptions is taken up in companion work[17,18] in which simulation results are compared with extensive and sensitive experimental data.

Equations 4–6 represent a complete description, within the limitations only of present knowledge, of all kinetic events that can alter free-radical concentrations in homogeneous and heterogeneous polymerizations. Aside from the issue of what values to assign to all the parameters that appear in these equations, the problem of how to make it possible to work with these equations must first

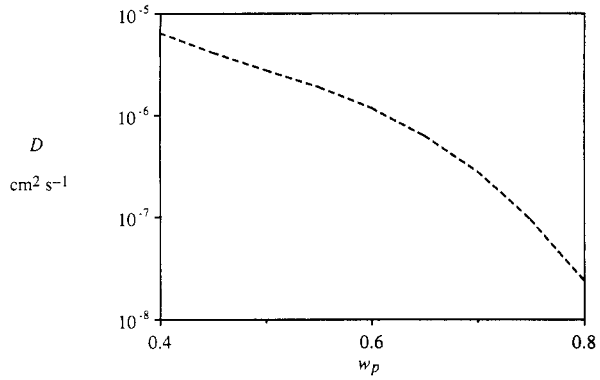

Figure 1. Dependence of monomer diffusion coefficient on weight fraction of polymer for styrene in polystyrene at 50 °C, using the functional form of eq 20. Range of w_p shown covers that relevant to emulsion polymerizations modeled in this study.

be overcome. Because all chain lengths are in principle possible, these equations theoretically form an infinite set of coupled differential equations. To render them tractable, it is therefore first necessary to truncate them at some reasonable chain length, i.e., to insist that all free radicals of degree of polymerization greater than some specified chain length be classified as one free-radical population. This chain length might, for example, be 5 times an average degree of polymerization in the system under study. Since, for an emulsion polymerization, average molecular weights are on the order of 10^6 and hence average degrees of polymerization of order 10^4, we still have an enormous set of coupled differential equations. The second step in making our set of equations tractable is therefore to "coarse-grain" them. This is acceptable (providing it is done sensibly—see below) because there is negligible difference, from a kinetic viewpoint, between, for example, a 1000-mer and a 1001-mer. Hence, in modeling kinetics these species may reasonably be treated as being identical and the population balance equations written accordingly. It is essential to realize that both the truncation and coarse-graining procedures are purely mechanical means of obtaining solutions of these equations to whatever accuracy is desired. Thus, in using these procedures, one would first establish grain-size and truncation conditions such that reducing the graining to smaller spacings and increasing the truncation length made no difference to the final results to within a prescribed tolerance (e.g., that the computed rate curve changes by no more than one part in 10^4). There are alternative numerical means of solving these equations (e.g., integral transform methods[26]), but they are less suited to the present requirements than the methods just described.

We therefore break the degrees of polymerization up into subdivisions Δ_I of grain size $|\Delta_I|$ monomer units. These widths will not all be equal: for example, Δ_1 might refer to monomeric free radicals only ($i = 1$), Δ_2 to $i = 2$ and 3, and Δ_{30} to all free radicals with degree of polymerization between 1000 and 1100. We define the coarse-grained variable P_I as

$$P_I = \sum_{i \in \Delta_I} T_i \approx T_I |\Delta_I| \tag{8}$$

where to good approximation I is any element of Δ_I: this approximation is only valid if T_i varies slowly as i varies within Δ_I (and indeed, the grain size in any actual calculation should be chosen so that this is the case). The truncation approximation means defining a P_n such that

$$P_n = \sum_{i \in \Delta_n} T_i \tag{9}$$

where Δ_n is of infinite width; i.e., Δ_n includes all chain lengths in excess of the largest chain length in Δ_{n-1}. For example, if a truncation chain length of 10 000 is chosen, then Δ_n spans i = 10 001 to ∞.

The truncated and coarse-grained approximations to eqs 4–6 are then

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \rho_A \delta_{1i} + k_{tr}[\mathrm{M}](\delta_{1i}(1 + \alpha\beta - \beta)\sum_{j=2}^{n} P_j - (1 - \delta_{1i})P_i) + \frac{(1 - \delta_{1i}) k_p{}^{i-1}[\mathrm{M}] P_{i-1}}{|\Delta_{i-1}|} - \frac{(1 - \delta_{1n}) k_p{}^{i}[\mathrm{M}] P_i}{|\Delta_i|} - 2P_i \sum_{j=1}^{n} c_{ij} P_j \tag{10a}$$

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = 2k_d f[\mathrm{I}]\delta_{1i} + k_{tr}[\mathrm{M}](\delta_{1i}\sum_{j=2}^{n} P_j - (1 - \delta_{1i})P_i) + \frac{(1 - \delta_{1i}) k_p{}^{i-1}[\mathrm{M}] P_{i-1}}{|\Delta_{i-1}|} - \frac{(1 - \delta_{1n}) k_p{}^{i}[\mathrm{M}] P_i}{|\Delta_i|} - 2P_i \sum_{j=1}^{n} k_t{}^{ij} P_j \tag{10b}$$

where the first coarse grain, Δ_1, obviously contains monomeric species, and $\delta_{ij} = 1$, $i = j$; $\delta_{ij} = 0$, $i \neq j$. Note that in eq 10 k_p has been allowed to be a function of subdivision number; i.e., a general dependence of k_p on chain length has been introduced. Equation 10 is now arbitrarily small in number. For example, with 40 suitably chosen chain-length subdivisions, we can accurately simulate the behavior of styrene polymerizations in which chains of a number-average degree of polymerization of 2×10^4 were produced: i.e., in our simulation there were only 40 coupled population balance differential equations.[17,18]

Equation 10 can also be obtained by a finite-difference approximation to the complete evolution equations when these are written in *integral* form, i.e., when the T_i are treated as a continuous function of the degree of polymerization. Denoting the continuous variable p as the degree of polymerization (and noting that strictly speaking p can only take the discrete values i = 1, 2, ... but that there are a very large number of values of i where T_i can take significant values—this is the justification necessary for valid introduction of a continuous degree of polymerization), we have the following continuum equivalent to eqs 4–6:

$$\frac{\partial T(p,t)}{\partial t} = \rho_A \delta(p) + k_{tr}[\mathrm{M}]\delta(p)\int_0^\infty T(p',t)\,\mathrm{d}p' - k_{tr}[\mathrm{M}]T(p,t) - k_p[\mathrm{M}]\frac{\partial T(p,t)}{\partial p} - 2T(p,t)\int_0^\infty c(p,p')\,T(p',t)\,\mathrm{d}p' \tag{11}$$

Note the following aspects of eq 11: for notational simplicity, we have let entry and transfer give rise to a chain of degree of polymerization $p = 0$ rather than $p = {}^1/_2$ or $p = 1$; also for simplicity, exit and reentry have been neglected; i.e., the above equation applies to (pseudo-bulk) emulsion systems in which either there is no exit ($\beta = 0$) or all desorbed free radicals reenter ($\alpha = 1$). Therefore, to obtain the homogeneous system analogue of eq 11, simply replace ρ with $2k_d f[\mathrm{I}]$ and $c(p,p')$ with $k_t(p,p')$; out of convenience we have assumed k_p to be totally chain-length independent; finally, in eq 10 $\delta(p)$ is the Dirac delta-function and $c(p,p')$ is the (pseudo-first-order) rate coefficient for termination between chains of degrees of polymerization p and p'. The only term in eq 11 that really requires explanation is that arising from propagation. In the discrete formulation, consider the contribution of propagation to dT_i/dt where $i > 1$; this contribution is

$$k_p[M](T_{i-1} - T_i) = k_p[M](-\Delta T_i/\Delta i) \qquad (12)$$

The propagation term in eq 11 follows clearly from eq 12.

Equation 10 is the finite difference approximation to eq 11 with the integrals evaluated by the most primitive method, viz., as sums of rectangles (in eqs 4–6 these rectangles are all of width one monomer unit). If desired, more computationally efficient forms can be obtained from eq 10 by better approximations to these integrals, for example by using Simpson's rule. Equation 11 will also be used later in this paper to develop alternative approximate forms of the population evolution equations. The coarse-graining and truncation techniques discussed above are in fact very efficient means specifically designed to solve these particular partial-differential equations numerically (since they are exactly equivalent to these equations in the limits of small grain size and large truncation size, limits which are always tested in numerical applications); while numerical solutions could alternatively be obtained by general-purpose partial-differential equation packages, the present method is custom-built for this purpose and therefore preferable to use of a general-purpose package.

3. Specification of Rate Parameters and Model Calculation

For our first model calculation to examine the behavior of the T_i, we shall now specify how the various rate parameters in eq 10 may be determined. It is emphasized that the following specifications are only illustrative; by no means are they expected to be generally applicable and thus are not an integral part of our general treatment (although the particular parameters chosen in fact successfully model sensitive experimental data[17,18]). Our illustrative calculation will be for an emulsion polymerization of styrene: the chosen conditions are those of the γ-relaxation of Adams et al.[14] at a weight fraction of 74% polymer. For this experiment the particle size was sufficiently large that radical exit may be ignored: i.e., $\beta = 0$, and thus the value of α is irrelevant. All k_t^{ij} were evaluated assuming termination to be diffusion-controlled. In this event the Smoluchowski equation can be used:

$$k_t^{ij} = 2\pi D_{ij}(r_i + r_j)N_A \qquad (13)$$

where D_{ij} is the mutual diffusion coefficient for species of degrees of polymerization i and j, respectively, and the separation at which termination is assumed to be instantaneous is $r_i + r_j$. Note that, as a consequence of how we define our termination rate coefficients in our rate equations, eq 13 applies for all pairs of i and j.

To specify $r_i + r_j$, consider first termination between two monomeric free radicals. This is clearly an event for which $r_i + r_j = \sigma$, where σ is the size of a monomer unit,[4] a value which is for the present purposes sufficiently close to the van der Waals radius for species of the size considered here). For reasons given in detail elsewhere,[17,18,27] this same relation should be a good approximation for termination between all chains. Hence, for the purposes of our exploratory calculations, we put

$$r_i + r_j = \sigma \qquad (14)$$

for all chain lengths i and j.

Next, consider the mutual diffusion coefficient D_{ij}. This is partitioned into a sum of contributions from each of the two species:

$$D_{ij} = D_i + D_j \qquad (15)$$

This is the case because obviously the rate at which species i diffuses is unaffected by the rate at which species j diffuses. It therefore remains to specify the self-diffusion coefficients D_i. In doing this it must be realized that in considering termination it is the rate of diffusion of the free-radical chain end, not the center of mass of the chain, that is of interest. Since free radicals are, in general, widely separated, the rapid small-length-scale motions of the free-radical chain end can be ignored in specifying D_i, for these will not serve to bring two widely separated free-radical chain ends any closer together; rather, only the longest-time-scale motion of the chain end need be considered. This motion has two sources. First, the chain end diffuses as the chain as a whole diffuses, a process characterized by a center-of-mass diffusion coefficient $D_{i,\mathrm{com}}$. Second, the chain end also diffuses by virtue of its nature as a site at which propagation occurs: this is reaction-diffusion,[2-4] the diffusion coefficient for which is denoted by "rd". Both these processes occur simultaneously; hence

$$D_i = D_{i,\mathrm{com}} + D_{i,\mathrm{rd}} \qquad (16)$$

An explicit model for this reaction-diffusion coefficient has been developed by the present authors.[4] As discussed by Russell et al.,[4] unless k_p is i-dependent, $D_{i,\mathrm{rd}}$ is chain-length independent. The only such i-dependence will be for very small chain lengths, at which it will be the case that $D_{i,\mathrm{com}} \geq D_{i,\mathrm{rd}}$. So, without any loss of accuracy the result of Russell et al.[4] for D_{rd} can be used for specifying $D_{i,\mathrm{rd}}$:

$$D_{i,\mathrm{rd}} = (1/6)k_p[M]a^2 \qquad (17)$$

where a is the root-mean-square end-to-end distance per square root of the number of monomer units in a polymer chain (i.e., in a random flight chain, a is the mean distance moved at each propagation step).

It remains to specify the chain-length variation of the center-of-mass diffusion coefficient, $D_{i,\mathrm{com}}$. For reasons discussed elsewhere,[17,18] experimental diffusion studies suggest that, for polymerizing systems beyond low conversions, $D_{i,\mathrm{com}} \propto M^{-1}$ for small M and $D_{i,\mathrm{com}} \propto M^{-2}$ for large M,[28] where M is the molecular weight of the polymer chain. Although the crossover from one diffusion regime to the other will be gradual in reality, it is assumed here that this transition occurs sharply at a particular degree of polymerization X_c. One thus obtains

$$\begin{aligned} D_{i,\mathrm{com}} &= D_{\mathrm{mon}}/i, \quad i \leq X_c \\ &= D_{\mathrm{mon}}X_c/i^2, \quad X_c < i \end{aligned} \qquad (18)$$

where D_{mon} is the diffusion coefficient of a monomeric species. In applying eq 18 to coarse-grained free-radical populations (i.e., those used in eq 10), the smallest i in Δ_I is used to calculate $D_{I,\mathrm{com}}$. Also, it is assumed that $D_{n,\mathrm{com}} = 0$, since our nth chain subdivision includes chains of up to infinite length; this is justified if the centers of mass of our longest chains are immobile on the time scale of reaction diffusion. This criterion can be used to set a truncation chain length for defining the nth chain subdivision.

The parameter values used for illustrative calculations are those for a styrene system at 50 °C: $k_p = 258$ dm^3 mol^{-1} s^{-1},[29,30] and k_{tr} from the literature value of $k_{tr}/k_p = 3.6 \times 10^{-5}$.[31] Next, we put

$$X_c = X_c^0/\phi_p \qquad (19)$$

where ϕ_p is the volume fraction of polymer, and the 100% polymer value X_c^0 is taken as 4. The following dependence of the diffusion coefficient of monomeric species on

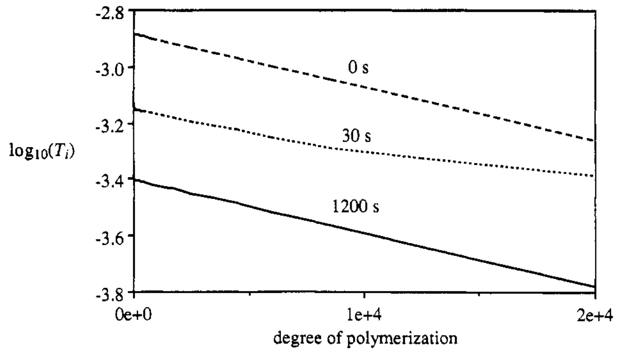

Figure 2. Calculated free-radical population as a function of degree of polymerization for a styrene emulsion polymerization under γ-radiolysis relaxation conditions at various times.

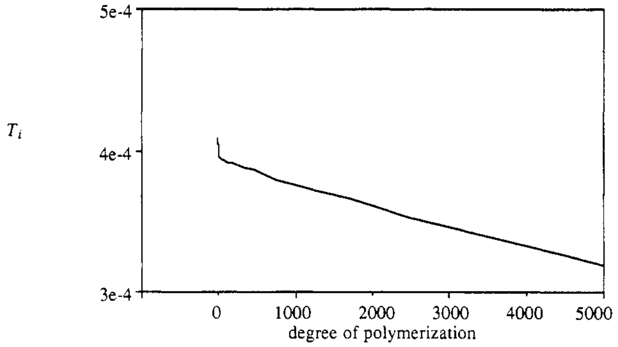

Figure 3. Populations of Figure 2 at 1200 s on an expanded (nonlogarithmic) scale for low degrees of polymerization.

weight fraction of polymer is used:

$$\log D_{\mathrm{mon}}\ (\mathrm{cm}^2\ \mathrm{s}^{-1}) = 0.417 - 29.51w_{\mathrm{p}} + 53.14w_{\mathrm{p}}^2 - 36.03w_{\mathrm{p}}^3 \quad (20)$$

which fits extant data[32-37] on diffusion coefficients in solvent/polystyrene systems over the range $0.4 \le w_{\mathrm{p}} \le 0.8$. This dependence of D_{mon} on w_{p} is shown in Figure 1.

With the above parameters, eq 10 was solved for conditions corresponding to a γ-radiolysis relaxation experiment where the initial $\bar{n}$ was 30, this high value resulting from the high value of ρ expected in a large-particle, high-radical-flux (γ-irradiated) system. At time zero, the value of ρ was reduced to $2.8 \times 10^{-2}\ \mathrm{s}^{-1}$, which is that typical for "background" thermal entry of the latex particles of this system.[14] That is, we are modeling a system as it relaxes from an initially high free-radical population; during this brief relaxation the monomor/polymer ratio decreases very little. As is commonly done, the initial radical populations P_I were calculated by taking T_i as being exponential in i. The time evolution of the radical population T_i is shown in Figure 2; the calculations shown therein have been checked for proper convergence in numerical parameters such as changing the intervals Δ_I, etc. Also, it was found that, after only a few seconds (of simulated polymerization time), virtually all populations are insensitive to the initial population distribution. It can be seen that in Figure 2 the radical population T_i decreases exponentially with i for higher i. Figure 3 reveals that this single-exponential variation is in fact restricted to higher degrees of polymerization: this figure shows a variation of T_i for small degrees of polymerization on an expanded, nonlogarithmic scale.

The exponential behavior of T_i for higher i is simply a consequence of the dominant macroradical chain-stopping and -starting mechanisms in the simulated system, being transfer (although the dominant radical loss mechanism is termination, the transfer rate $k_{\mathrm{tr}}[\mathrm{R}^\bullet][\mathrm{M}]$ greatly exceeds the termination rate $\sum\sum k_{\mathrm{t}}^{ij}[\mathrm{R}^\bullet_i][\mathrm{R}^\bullet_j]$ in the present system). The distribution function for growing chains, if transfer is the *only* chain-stopping and -starting mechanism, is[38] $\exp(-k_{\mathrm{tr}}M/k_{\mathrm{p}}M_0)$, where M_0 is the molecular weight of monomer. The slope of the straight-line region in Figure 2 (in which T_i is plotted against $i = M/M_0$) is indeed very close to $-k_{\mathrm{tr}}/k_{\mathrm{p}}$: this is merely a check on the correctness of our computer code. What is noteworthy is that, for low degrees of polymerization, the distribution of T_i is not exponential in the way it is at higher i: indeed, this distribution decreases at very small i much faster than it does at larger i. This indicates that at small i chain-stopping and -starting events other than transfer are kinetically significant. This is very important for the kinetics, since (as will be seen) the dominant means of termination in our system is between long chains and chains of a small degree of polymerization; hence, one cannot simplify the kinetic treatment by assuming a single-exponential distribution for T_i, as is sometimes done (e.g., in ref 11).

Having established a methodology for obtaining exact solutions to the evolution equations for the chain-length distribution of macroradicals, we now use this to derive and test approximate solutions.

4. Simple Approximate Solutions

Equations 4–6 are a complete prescription for the time evolution of the T_i; unfortunately, although (in the form of eq 10) they can be readily solved numerically, this does require significant computational resources (e.g., sufficient to enable the numerical solution to 50 stiffly-coupled ordinary differential equations to be obtained). We now make a series of assumptions which allow solutions to be computed easily and quickly and in a manner that can be used for routine fitting and interpretation of experimental data.

Preparatory to detailing these simplifying assumptions, we note that for conceptual convenience macroradicals can be approximately categorized as being either *short* or *long*. Short chains have a chain length less than or equal to some degree of polymerization z; they are comparatively mobile by virtue of their relatively unhindered (center-of-mass) translational diffusion. Long chains have a degree of polymerization greater than z and are much less mobile; their chain ends can be thought of as moving (on the time scales of interest) entirely by reaction diffusion. For a well-chosen value of z (details follow), most chains are long. Thus, providing z is not too small, most termination events will be between a short chain and a long one, while a much smaller percentage of termination events will involve two long chains. Terminations between two short chains will occur with a high rate coefficient, but the relatively low number of small chains means that these short/short events are kinetically unimportant. We note, however, that (given a functional form for the diffusion coefficient of oligomeric species as a function of both their degree of polymerization and the weight fraction of polymer) the value of z will turn out to be a parameter whose value is formally chosen purely to facilitate numerical solutions of the evolution equations, although this value must in actuality not be less than that of the degree of polymerization for entanglement of a chain.

In finding a more tractable form for our evolution equations, all the approximations inherent in eqs 4–6 are retained. In addition, the following assumptions are now made:

(1) In the terms involving transfer in eqs 4a and 4b, the quantity $k_{\mathrm{tr}}[\mathrm{M}](\sum T_i - T_1)$ will be approximated by $k_{\mathrm{tr}}[\mathrm{M}]\sum T_i$. Of course, transfer to monomer of monomeric

free radicals yields a monomeric free radical, and hence monomeric free radicals are neither gained nor lost by such transfer, but since $T_1 \ll \sum T_i$, no loss of accuracy is incurred by this approximation.

(2) The contribution of termination to $\mathrm{d}T_i/\mathrm{d}t$, which involves a summation over all species j, is assumed to depend *only* on i: i.e., k_t^{ij} is assumed to vary only with i and not with j, where j is a radical of any length. This assumption enables the termination summation quantity $\sum c_{ji}T_j$ in eqs 4a, 5a, and 6a to be replaced simply by a term which we denote $c_{iL}\bar{n}$ (and similarly for the equivalent quantity in eqs 4b, 5b, and 6b). Here the subscript L denotes "long": i.e., we assume that the termination rate coefficient between an i-mer and any other species can be replaced by that between an i-mer and a long species. This is not equivalent to assuming that termination between any two short species is negligible; rather, it means that any short/short termination rate coefficient is assumed to be the same as that for termination between a short and a generic long species. Now, long species are effectively immobile, and thus the rate coefficient for termination between two short species differs from that between the short species and any long species whatsoever by a factor of 2 at most (see eqs 13 and 15). Since the total number of short chains is comparatively small (see Figure 2), this approximation should be a good one to calculate the time dependence of the overall conversion (although it may give inaccuracies in individual termination rates between species of different lengths). This is because the termination rate is dominated by short/long termination events, and the rate coefficient for such events is essentially determined entirely by the length of the short species.

Given these assumptions, eqs 4–6 become

$$\mathrm{d}T_1/\mathrm{d}t = \rho_A + k_{tr}[M]\bar{n}(1-\beta+\alpha\beta) - k_p^{1}[M]T_1 - 2T_1c_{1L}\bar{n} \quad (21a)$$

$$\mathrm{d}T_1/\mathrm{d}t = 2k_d f[I] + k_{tr}[M][R^\bullet] - k_p^{1}[M]T_1 - 2T_1k_t^{1L}[R^\bullet] \quad (21b)$$

$$\mathrm{d}T_2/\mathrm{d}t = -k_{tr}[M]T_2 + k_p^{1}[M]T_1 - k_p[M]T_2 - 2T_2c_{2L}\bar{n} \quad (22a)$$

$$\mathrm{d}T_2/\mathrm{d}t = -k_{tr}[M]T_2 + k_p^{1}[M]T_1 - k_p[M]T_2 - 2T_2k_t^{2L}[R^\bullet] \quad (22b)$$

$$\mathrm{d}T_i/\mathrm{d}t = -k_{tr}[M]T_i + k_p[M](T_{i-1} - T_i) - 2T_ic_{iL}\bar{n}, \quad i > 2 \quad (23a)$$

$$\mathrm{d}T_i/\mathrm{d}t = -k_{tr}[M]T_i + k_p[M](T_{i-1} - T_i) - 2T_ik_t^{iL}[R^\bullet], \quad i > 2 \quad (23b)$$

The major difference between eqs 4–6 and 21–23 is that, whereas in eqs 4–6 any particular T_i depends on all other T_i, in eqs 21–23 the only other population that a T_i depends on is T_{i-1}. This situation has been brought about by the second of the above approximations, which significantly decouples the population balance equations, eqs 4–6. Equations 4–6 are not especially novel (indeed, they were essentially written down by Benson and North[1]), but eqs 21–23 are new. It will now be shown how easy eqs 21–23 are to work with and that they are a very accurate approximation to eqs 4–6.

Recalling our conceptual categorization of macroradicals into short and long species, we proceed by making the steady-state approximation ($\mathrm{d}T_i/\mathrm{d}t = 0$) for all T_i with $i \le z$; i.e., the populations of all short free radicals are assumed to be in pseudo-steady-state. Equations 21–23 can now be rearranged to give

$$T_1 = \frac{\rho_A + k_{tr}[M]\bar{n}(1-\beta+\alpha\beta)}{k_p^{1}[M] + 2c_{1L}\bar{n}} \quad (24a)$$

$$T_1 = \frac{2k_d f[I] + k_{tr}[M][R^\bullet]}{k_p^{1}[M] + 2k_t^{1L}[R^\bullet]} \quad (24b)$$

$$T_2 = \frac{k_p^{1}[M]T_1}{k_p[M] + k_{tr}[M] + 2c_{2L}\bar{n}} \quad (25a)$$

$$T_2 = \frac{k_p^{1}[M]T_1}{k_p[M] + k_{tr}[M] + 2k_t^{2L}[R^\bullet]} \quad (25b)$$

$$T_i = \frac{k_p[M]T_{i-1}}{k_p[M] + k_{tr}[M] + 2c_{iL}\bar{n}}, \quad i = 3, ..., z \quad (26a)$$

$$T_i = \frac{k_p[M]T_{i-1}}{k_p[M] + k_{tr}[M] + 2k_t^{iL}[R^\bullet]}, \quad i = 3, ..., z \quad (26b)$$

Given a value of $\bar{n}$ (or $[R^\bullet]$), eqs 24–26 can be trivially solved (by starting with eq 24 for T_1, finding T_2 from eq 25, etc.). As an alternative to such iterative computation, eqs 24–26 can be rearranged to give analytic expressions for T_i (for brevity, only that for $i = 3$–z in the homogeneous system case is given; the analogues to eqs 24–26a are obvious from eq 27). Because the numerator and denominator in eq 27 become very large as i mounts, eqs 24–26 are used in computational evaluations of T_i in order to avoid numerical overflow problems.

$$T_i = \frac{(2k_d f[I] + k_{tr}[M][R^\bullet])k_p^{1}[M](k_p[M])^{i-2}}{(k_p^{1}[M] + 2k_t^{1L}[R^\bullet])\prod_{j=2}^{i}(k_p[M] + k_{tr}[M] + 2k_t^{jL}[R^\bullet])}, \quad i = 3, ..., z \quad (27)$$

The accuracy of eqs 24–26 was checked by comparison of the predictions of eqs 24a, 25a, and 26a with values of T_i from Figure 2, which were generated by numerical solution of eq 10 and so can be considered as being exact. It was found that, for $i = 1$–5 inclusive, the above equations gave values of T_i identical (to four significant figures or better) to those for 30 and 1200 s from Figure 2. It must be mentioned that the 30-s data of Figure 2 correspond to a non-steady-state polymerization (in γ-relaxation a system passes from an "in-source" pseudo-steady state to an "out-of-source" or thermal pseudo-steady state), while the 1200-s data correspond to a system in a (pseudo-)steady state. This strongly suggests that our method for calculating T_i is accurate under steady-state and non-steady-state polymerization conditions alike.

Having established how to calculate T_i accurately for i less than or equal to an arbitrarily chosen value z, it remains to deal with the T_i for which $i > z$. Here we make a final approximation: we group together as a single radical population P all free radicals of degree of polymerization greater than z. From eq 3, the value of $\bar{n}$ (or $[R^\bullet]$) is thus

$$\bar{n} = \sum_{i=1}^{\infty} T_i = \sum_{i=1}^{z} T_i + \sum_{i=z+1}^{\infty} T_i \equiv \sum_{i=1}^{z} T_i + P \quad (28)$$

Provided z is not too small, all P species will be entangled

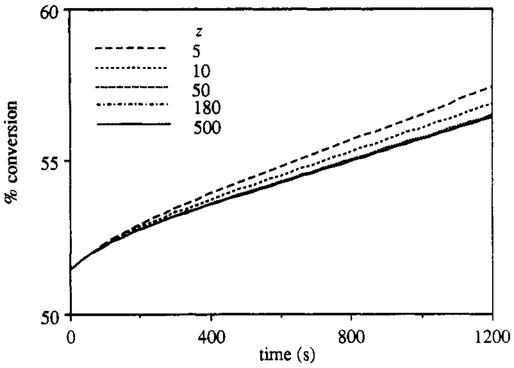

Figure 4. Conversion versus time as a function of z, calculated using eq 29a. Conversion is given in terms of percent conversion of monomer into polymer, with the initial conversion taken from the reference experiment of Adams et al.[14] Results for z = 180 and 500 are indistinguishable on this scale.

and thus long. We therefore assume that termination between any two P species is by reaction diffusion, i.e., that there is no center-of-mass diffusion of such chains on the time scale of reaction diffusion. Hence, from eqs 13–15 and 17, the rate coefficient for termination between *any* two P species is independent of the degree of polymerization of each chain. Given this, eq 6 may be summed over all $i > z$ to yield

$$\mathrm{d}P/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{M}]T_z - k_{\mathrm{tr}}[\mathrm{M}]P - 2c_{\mathrm{LL}}P^2 - 2P\sum_{i=1}^{z} c_{i\mathrm{L}}T_i \qquad (29\mathrm{a})$$

$$\mathrm{d}P/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{M}]T_z - k_{\mathrm{tr}}[\mathrm{M}]P - 2k_{\mathrm{t}}^{\mathrm{LL}}P^2 - 2P\sum_{i=1}^{z} k_{\mathrm{t}}^{i\mathrm{L}}T_i \qquad (29\mathrm{b})$$

where the long/long termination rate coefficient is the so-called rigid-chain residual termination rate coefficient[4]

$$k_{\mathrm{t}}^{\mathrm{LL}} = (2/3)\pi k_{\mathrm{p}}[\mathrm{M}]a^2\sigma \qquad (30)$$

and c_{LL} follows from eq 7.

The appropriate version of eq 29 can be used in the fashion now explained to model a polymerization. If the overall radical population is known, all the T_i that appear in eq 29 can be calculated from eqs 24–26. The difficulty here is that, in this modeling, the overall free-radical population is not a known quantity but is evaluated as part of the modeling process. This problem is easily overcome computationally, as follows. Given a value of P (e.g., by the call to the right-hand-side-generating subroutine in a numerical solution of coupled differential equations), the starting approximation $\bar{n}$ (or $[\mathrm{R}^\bullet]$) = P is made. This enables calculation of the T_i, from which a more accurate value of $\bar{n}$ (or $[\mathrm{R}^\bullet]$) can be calculated using eq 28. Better values of T_i can then be evaluated, and so on. This procedure is iterated until convergence, at which point the final values of T_i obtained may be substituted into eq 29, the numerical solution of which may then proceed.

The problem of specifying a value of z is now addressed. Given a functional form for D_i, this is in fact just a numerical parameter whose value is best established by carrying out some sample calculations in which successively larger values of z are tried until convergence of an overall kinetic parameter (e.g., conversion) is achieved. This is illustrated in Figure 4, in which are shown conversion–time results from simulations in which the parameters of section 3 were used. Given that the z = 180 and z = 500 results are indistinguishable in Figure 4, it is clear that, by z = 180, convergence has been attained; i.e., using a larger value of z makes negligible difference to the simulated kinetics.

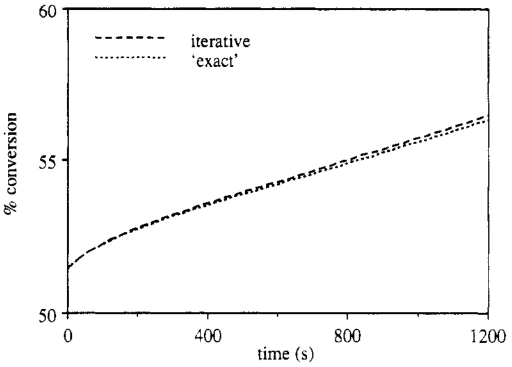

Figure 5. Comparison of predictions of eq 29a ("iterative") (with z = 180) with those of eqs 10 ("exact") from section 3.

Having established how to specify z, it remains to test whether the mathematical approximations of this section provide an accurate description of the "true" kinetics. This is done in Figure 5 by comparing the z = 180 data of Figure 4 with the conversion–time profile calculated in the simulation of section 3. In this latter simulation a set of about 40 coupled population-balance differential equations (corresponding to a coarse-grained distribution of the T_i) were solved numerically, whereas in the simulations of the present section, it was necessary to solve numerically only one population-balance differential equation (eq 29a). The simulations whose results appear in Figure 5 involve identical parameter sets: i.e., this is a direct "theory-versus-theory" comparison. It is clear from Figure 5 that the methodology of this section succeeds admirably in reproducing the results of the simulation in which eq 10 (i.e., essentially the complete free-radical evolution equations) was used. In fact, it should be noted that, due to the way in which $D_{I,\mathrm{com}}$ values were evaluated in section 3 (see eq 18 and related text), the simulation of that section actually overestimated the exact rate of termination and so gave lower than exact conversions. Thus it appears the (large z) simulations of this section may be better approximations to the exact kinetics than the simulation of section 3 (the exactness of the section 3 simulation can be improved by finer coarse-graining of the free-radical population).

In view of the accuracy of the methodology of this section, the following easier but less precise way of solving eq 29 is pointed out: if z is not too large, most macroradicals are P species, and so one has $\bar{n}$ (or $[\mathrm{R}^\bullet]$) $\approx P$. Hence, eq 29 may be approximated by

$$\mathrm{d}\bar{n}/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{M}]T_z - k_{\mathrm{tr}}[\mathrm{M}]\bar{n} - 2c_{\mathrm{LL}}\bar{n}^2 - 2\bar{n}\sum_{i=1}^{z} c_{i\mathrm{L}}T_i \qquad (31\mathrm{a})$$

$$\mathrm{d}[\mathrm{R}^\bullet]/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{M}]T_z - k_{\mathrm{tr}}[\mathrm{M}][\mathrm{R}^\bullet] - 2k_{\mathrm{t}}^{\mathrm{LL}}[\mathrm{R}^\bullet]^2 - 2[\mathrm{R}^\bullet]\sum_{i=1}^{z} k_{\mathrm{t}}^{i\mathrm{L}}T_i \qquad (31\mathrm{b})$$

Now no iterative procedure is needed to calculate the overall macroradical population, since this quantity is obtained directly by solving eq 31. Thus computational solution of eq 31 is even quicker than that of eq 29. The accuracy of this latest approximation was tested by comparing numerical solutions to eq 31a (with z = 180) with the equivalent solutions to eq 29a. This comparison is shown in Figure 6. This latest approximation results in lower conversions (because the overall radical population

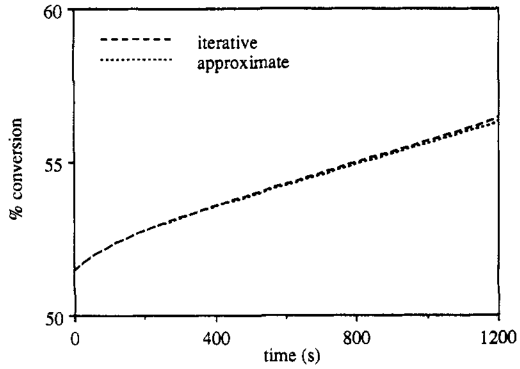

Figure 6. Comparison of predictions of eq 29a ("iterative") with those of eq 31a ("approximate") ($z = 180$ used in both calculations).

is underestimated) but by such a small amount that the approximation is well justified.

Equations 24–26 and 29 (or 31) are our required simpler form of the free-radical evolution equations. This simpler form consists of only a *single* differential equation (eq 29 or 31), with the T_i therein obtained by direct substitution into eqs 24–26, starting at eq 24. Numerical solution of this single differential equation is straightforward and results in considerable savings of computer time with no loss of accuracy. Evaluation of the hierarchical equations, eqs 24–26, should strictly be carried out for every value of i between 1 and z. While this latter process is not at all computationally demanding, it can be accelerated by using the same coarse-graining technique as was used in deriving eq 10. Lastly, recall that in our new evolution equations z is a purely numerical parameter whose appropriate value should be determined by finding the smallest value (this minimizes computation time) which gives acceptably similar kinetics to the kinetics obtained with larger values. For the termination model of section 3, a model suited to intermediate- and high-conversion polymerizations, a value of z in the range 100–200 has been found to be perfectly adequate. Work in progress indicates that the methodology of this section may be used for modeling low-conversion polymerizations (although under some circumstances it may be necessary to modify approximation 2), but the different values of k_t^{ij} that apply at such conversions necessitate the use of a higher z in such modeling.

It is significant that eq 31, our new population evolution equation, although simple, is quite different in form to the basic (pseudo)bulk relation, eq 2 (which is also a single differential equation description of the free-radical population evolution in a polymerization). The latter was derived from a coarse overall consideration of the kinetics, while our new equation stems from a more subtle microscopic treatment of the entire range of kinetic events. Despite this, solution of the new equation, which explicitly takes into account chain-length-dependent processes, requires essentially no more computational resources than solution of the bulk equation.

Although the tests of the approximate mathematical treatment given in this section have all been for a styrene emulsion polymerization, extensive calculations on a corresponding methyl methacrylate system[17,18] (which inter alia shows a strong gel effect) show that the general conclusions given in this section also hold true for this rather different monomer.

5. Alternative Short-Long Equations

Equations 24–26 and 29 constitute a complete and accurate account of chain-length-dependent polymerization kinetics, with the length of each macroradical taken explicitly into account as necessary. It is of interest to compare these equations with an alternative, and more primitive, chain-length treatment that we have given previously.[14] In this more primitive treatment, the radical population was divided into only two sorts of chains, short and long, without any further subdivision. For an emulsion system one thus puts

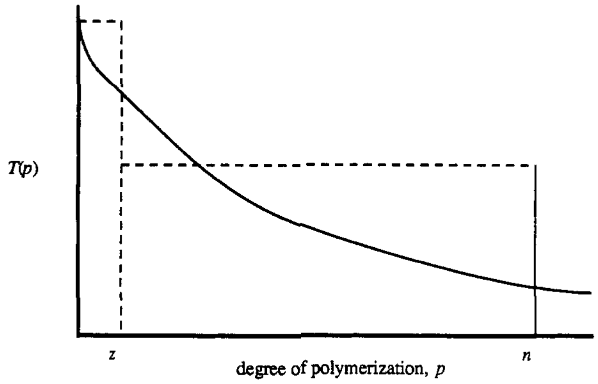

Figure 7. Representation of the chain-length distribution of macroradicals as two tophat functions.

$$\bar{n} = \bar{s} + \bar{l} \tag{32}$$

where $\bar{s}$ and $\bar{l}$ are respectively the populations of generic short and long chains (i.e., the average number of short and long chains, respectively, per latex particle). The following differential equations for the evolution of these quantities can then be written down, these being an extension of eq 2a:[14]

$$d\bar{s}/dt = \rho_A + k_{tr}[M]\bar{l} - (1/z)k_p[M]\bar{s} - 2c_{SS}\bar{s}^2 - 2c_{SL}\bar{s}\bar{l} \tag{33}$$

$$d\bar{l}/dt = (1/z)k_p[M]\bar{s} - k_{tr}[M]\bar{l} - 2c_{SL}\bar{s}\bar{l} - 2c_{LL}\bar{l}^2 \tag{34}$$

where z is once again the critical degree of polymerization at which short chains are deemed to become long ones (and so in this model z has an apparent physical meaning—it was originally envisaged as being the length at which a growing chain became entangled—rather than just being a numerical parameter), and the subscripts S and L denote events between short and long species. For simplicity, any contributions of exit and reentry (which would result in additional terms in eq 33) have been ignored; the homogeneous system analogues to eqs 33 and 34 are sufficiently obvious that they are not explicitly given. The above equations have been used with some success to interpret experimental data.[14] While these equations can now be regarded as a primitive approximation to the complete population evolution equations deduced in section 2 (eqs 33 and 34 are just eq 10 with $n = 2$) and section 4 (eq 34 is eq 29 with $T_z = \bar{s}/z$ and all short/long termination rate coefficients replaced by a single short/long termination rate coefficient), it is of interest to examine under what approximations eqs 33 and 34 can be derived from the complete continuum equation, eq 11.

To begin, we approximate the distribution function $T(p)$ of eq 11 as the sum of two "tophat" functions (Figure 7)

$$T(p) \approx \bar{s}(t)\, T_S(p) + \bar{l}(t)\, T_L(p) \tag{35}$$

where $T_S(p)$ and $T_L(p)$ are tophat functions of unit area

$$T_S(p) = 1/z, \quad 0 \le p < z; \qquad T_S(p) = 0, \quad \text{otherwise} \tag{36}$$

$$T_L(p) = 1/(n - z), \quad z \le p < n; \qquad T_L(p) = 0, \quad \text{otherwise} \tag{37}$$

and the quantities $\bar{s}(t)$ and $\bar{l}(t)$ are to be determined.

Equation 35 is now used to derive an expression for the left-hand side of eq 11, while eqs 36 and 37 are substituted into the right-hand side of eq 11. The resulting equation is multiplied by $T_S(p)$ and integrated over all p (i.e., from zero to infinity) to obtain eq 41, while it is multiplied by $T_L(p)$ and integrated over all p to obtain eq 42. To derive eqs 41 and 42, a number of algebraic manipulations need to be carried out, these using the following results. First

$$T_S(p) = \frac{1}{z}[S(p) - S(p-z)] \qquad (38)$$

$$T_L(p) = \frac{1}{n-z}[S(p-z) - S(p-n)] \qquad (39)$$

where the unit step function is defined by $S(x) = 1$, $x \geq 0$; $S(x) = 0$, $x < 0$. The differential of the step function required in the substitution into eq 10 is given by

$$\mathrm{d}S(x)/\mathrm{d}x = \delta(x) \qquad (40)$$

The algebra of these operations on eq 11 is relatively straightforward but tedious, and the final results are that eq 11 becomes

$$\frac{\mathrm{d}\bar{s}}{\mathrm{d}t} = \rho_A + k_{tr}[\mathrm{M}]\bar{l} - \frac{1}{z}k_p[\mathrm{M}]\bar{s} - 2\bar{s}^2\frac{1}{z^2}\int_0^z \mathrm{d}p \int_0^z \mathrm{d}p'\, c(p,p') - 2\bar{s}\bar{l}\frac{1}{z(n-z)}\int_0^z \mathrm{d}p \int_z^n \mathrm{d}p'\, c(p,p') \qquad (41)$$

$$\frac{\mathrm{d}\bar{l}}{\mathrm{d}t} = \frac{1}{z}k_p[\mathrm{M}]\bar{s} - k_{tr}[\mathrm{M}]\bar{l} - \frac{1}{n-z}k_p[\mathrm{M}]\bar{l} - \frac{2\bar{s}\bar{l}}{z(n-z)}\int_0^z \mathrm{d}p \int_z^n \mathrm{d}p'\, c(p,p') - 2\bar{l}^2\frac{1}{(n-z)^2}\int_z^n \mathrm{d}p \int_z^n \mathrm{d}p'\, c(p,p') \qquad (42)$$

Equation 41 is clearly the same as eq 33, while eq 42 is only identical to eq 34 in the limit of the chain length n being infinite. This just means that L species can be of any degree of polymerization upward of z, i.e., that L species cannot be lost by propagation. Since this has been implicitly assumed in writing eqs 32–34, eqs 33 and 34 can truly be said to follow from eq 11 when the indicated approximations are made.

Comparing eqs 41 and 42 with eqs 33 and 34, one can identify expressions for the so-called short/short, short/long, and long/long termination rate coefficients. This is useful because eqs 33 and 34 by themselves do not indicate how these coarse-grained termination rate coefficients are related to precise, microscopic termination rate coefficients. Of particular interest is the (pseudo-first-order) short/long termination rate coefficient c_{SL} (or equivalently the second-order rate coefficient k_t^{SL}), which clearly is

$$k_t^{SL} = \frac{1}{z(n-z)}\int_0^z \mathrm{d}p \int_z^n \mathrm{d}p'\, k_t(p,p') \qquad (43)$$

It can be safely assumed that $k_t(p,p')$ is independent of p' for $p' > z$: i.e., the rate coefficient for termination between a long and a short chain is independent of the length of the long chain. The physical arguments for this assumption have been discussed in section 3. Putting $k_t(p,p') = k_t^L(p)$, $p' > z$, and $p < z$, one then obtains from eq 43 that

$$k_t^{SL} = \frac{1}{z}\int_0^z k_t^L(p)\,\mathrm{d}p \qquad (44)$$

We now adopt eqs 13–17 for $k_t^L(p)$ and note that the center-of-mass diffusion coefficient of the L species is essentially zero; hence

$$k_t^L(p) = 2\pi\sigma\left(\frac{1}{6}k_p[\mathrm{M}]a^2 + D(p)\right) + 2\pi\sigma\left(\frac{1}{6}k_p[\mathrm{M}]a^2\right) \qquad (45)$$

where $D(p)$ is the center-of-mass diffusion coefficient of a chain of degree of polymerization p, the first $(^1/_6)k_p[\mathrm{M}]a^2$ term is the reaction-diffusion contribution to the diffusion of a short chain, and the second is the same quantity for a long chain (reaction diffusion being the fastest mode of diffusion of the end of a long chain). Equation 18 can be generalized by writing $D_{i,\mathrm{com}} \equiv D(p) = D_{\mathrm{mon}}g(p)$; one then has

$$k_t^{SL} = 2\pi\sigma\left(\frac{1}{3}k_p[\mathrm{M}]a^2 + \frac{D_{\mathrm{mon}}}{z}\int_0^z g(p)\,\mathrm{d}p\right) \qquad (46)$$

If it is assumed that the center-of-mass diffusion coefficient of a short species is inversely proportional to its chain length, then $g(p) = 1/(p + {}^1/_2)$ (this is because p begins at 0 and so $p = {}^1/_2$ is equivalent to a 1-mer). Substituting this expression into eq 46, one obtains

$$k_t^{SL} = 2\pi\sigma\left(\frac{1}{3}k_p[\mathrm{M}]a^2 + \frac{D_{\mathrm{mon}} \ln(2z+1)}{z}\right) \qquad (47)$$

This equation has previously been derived by us by alternative means.[14]

Equation 47 above has been derived here simply to illustrate how the equations of this section may be put to use. At this stage these equations will not be explored any further, although it is felt that eq 11 may prove to be of future use in describing polymerizations. This is because, as illustrated above, the integrals introduced by eq 11 may be amenable to analytic evaluation where the summations of eq 10 are not.

6. Conclusion

Modeling of a free-radical polymerization involves calculating an overall rate of termination, a process characterized by an *average* termination rate coefficient $\langle k_t \rangle$, as expressed in eq 2b. In the notation of this paper

$$\langle k_t \rangle = \frac{\sum_i \sum_j T_i T_j k_t^{ij}}{(\sum_i T_i)^2} \qquad (48)$$

Equation 48 was explicitly stated by Allen and Patrick.[39] One of the problems this paper has addressed is that of using eq 48 to model polymerizations. In broad terms, the difficulty here is 2-fold. First, the microscopic termination rate coefficients k_t^{ij} must be specified, and, second, the microscopic free-radical populations T_i must be known. The second problem is the more troublesome, for most workers have had little difficulty in proposing models for k_t^{ij}, whereas few have properly converted k_t^{ij} values into $\langle k_t \rangle$ values so that eq 2b will exactly model the kinetics. The present paper has shown both how to find the T_i required to evaluate eq 48 for use in eq 2 and, even more importantly, how to replace the oversimple evolution equations which take no account of chain length, eq 2, by ones which do while being no more difficult to solve numerically.

In this paper we have taken physically reasonable k_t^{ij} values (section 3) and investigated how to use these to predict accurately and efficiently the overall kinetics. In other words, we have addressed the problem of calculating the radical population distribution T_i. In sections 2 and 3 this was done essentially by brute force: the complete radical evolution equations (eqs 4–6) were truncated and coarse-grained to yield a tractable set (eq 10), numerical solutions to which were then computed. Inspection of these solutions (section 3) led to insights which enabled the complete evolution equations to be rewritten (section 4) in a form (eqs 24–26 and 29) involving a single radical-evolution differential equation (eq 29, subsequently approximated as eq 31). This very convenient approximation, nevertheless, explicitly incorporates chain-length-dependent termination rate coefficients. Also, by comparison of its predictions with those of the exact treatment, we have shown the single-equation formulation to be extremely accurate in its predictions of T_i and hence in its predictions of overall kinetics (section 4). In a final section of work (section 5), the utility of the continuum free-radical population evolution equations (eqs 11) was illustrated by deriving from them the so-called short/long pseudobulk emulsion polymerization equations (eqs 33 and 34). The application of the results of the present paper to detailed interpretation of sensitive experimental data dominated by termination events will be presented in a subsequent publication.[18]

Finding definitive answers to well-known and basic questions concerning free-radical polymerization kinetics has proved to be very difficult. Such questions include what precisely is the origin of the so-called Trommsdorff–Norrish or "gel" effect (as it occurs in both emulsion and bulk polymerizations; this will clearly depend strongly on the dependence of the diffusion coefficient of an oligomer on its degree of polymerization and on the weight fraction of polymer, both of which incorporate such factors as the critical chain length for entanglement) and how polymerizations could be conducted so as to minimize the residual monomer content of product polymers. A major reason for these questions remaining unanswered is that a tractable methodology for understanding polymerizations at a microscopic level has been slow to emerge. The findings of this paper suggest that certainly for intermediate- and high-conversion polymerizations, such a methodology may now have been developed. It is therefore hoped that this work will lead to a microscopic understanding of polymerizations to yield answers to basic kinetic questions.

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References and Notes

(1) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935.
(2) Schulz, G. V. *Z. Phys. Chem. (Munich)* **1956**, *8*, 290.
(3) Gardon, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2853.
(4) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2133.
(5) Cardenas, J.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1883.
(6) Cardenas, J.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 883.
(7) Casey, B. S.; Maxwell, I. A.; Morrison, B. R.; Gilbert, R. G. *Makromol. Chem., Macromol. Symp.* **1990**, *31*, 1.
(8) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(9) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1299.
(10) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Macromolecules* **1987**, *20*, 839.
(11) Bamford, C. H. *Eur. Polym. J.* **1989**, *25*, 683.
(12) Mahabadi, H. K. *Macromolecules* **1985**, *18*, 1319.
(13) Mahabadi, H. K. *Macromolecules* **1991**, *24*, 606.
(14) Adams, M. E.; Russell, G. T.; Casey, B. S.; Gilbert, R. G.; Napper, D. H.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624.
(15) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2141.
(16) Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3225.
(17) Russell, G. T. Thesis, University of Sydney, 1990.
(18) Russell, G. T.; Gilbert, R. G.; Napper, D. H., manuscript in preparation.
(19) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.
(20) Ballard, M. J.; Gilbert, R. G.; Napper, D. H. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 533.
(21) Gilbert, R. G.; Napper, D. H. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1983**, *23*, 127.
(22) Normufa, M. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic: New York, 1982.
(23) Ugelstad, J.; Hansen, F. K. *Rubber Chem. Technol.* **1976**, *49*, 536.
(24) Napper, D. H.; Gilbert, R. G. In *Comprehensive Polymer Science*; Allen, G. A., Bevington, J. C., Eastwood, G. C., Eds.; Pergamon: Oxford, 1989; Vol. 4; p 171.
(25) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629.
(26) Sneddon, I. H. *The Use of Integral Transforms*; McGraw-Hill: New York, 1972.
(27) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific: Oxford and Cambridge, MA, 1990.
(28) Tirrell, M. *Rubber Chem. Technol.* **1984**, *57*, 523.
(29) Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 293.
(30) Hawkett, B. S.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1323.
(31) Tobolsky, A. V.; Offenbach, J. *J. Polym. Sci.* **1955**, *16*, 311.
(32) Berens, A. R.; Hopfenberg, H. B. *J. Membr. Sci.* **1982**, *10*, 283.
(33) Landry, M. R.; Gu, Q. *Macromolecules* **1988**, *21*, 1158.
(34) Kosfeld, R.; Goffloo, K. *Kolloid Z. Z. Polym.* **1971**, *247*, 801.
(35) Lee, J. A.; Frick, T. S.; Huang, W. J.; Lodge, T. P.; Tirrell, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 369.
(36) Goffloo, K.; Kosfeld, R. *Angew. Chem., Makromol. Chem.* **1974**, *37*, 105.
(37) Zhang, J.; Wang, C. H. *Macromolecules* **1988**, *21*, 1811.
(38) Lichti, G.; Gilbert, R. G.; Napper, D. H. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic: New York, 1982.
(39) Allen, P. E. M.; Patrick, C. R. *Makromol. Chem.* **1961**, *47*, 154.