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Autoacceleration in Free Radical Polymerization. 1. Conversion

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ABSTRACT: We present a theory of the "autoacceleration" of polymerization rates during free radical polymerization, known as the Trommsdorff or "gel" effect. The starting point is recent theory of polymer–polymer reaction kinetics, according to which the termination rate constant between two macroradicals ("living chains") is dominated by the length N of the shortest chain, $k_t \sim N^{-\alpha}$. At lower conversions, when $\alpha < 1$, we show that it is justified to preaverage k_t over the living population. Autoacceleration results from a transition to entanglement-dominated kinetics in which short chain domination is so strong as to be unintegrable, i.e., $\alpha > 1$. This invalidates preaveraging. Net termination rates are then dominated by short–long events; long chain mobility is so reduced by entanglements that short mobile chains provide a faster termination mechanism despite their small numbers. This leads to results very different from those of the classical Flory theory. We find polymerization rates are independent of initiation rates R_i, in contrast to the classical $\sqrt{R_i}$ result, while mean living chain length $\bar{N} \sim 1/R_i$. Initially, polymer conversion ϕ grows with a characteristic power or finite time singularity, and for polymerizations above the glass temperature the approach to completion is hyperbolic in time, $1 - \phi \sim \tau_{auto}/t$ where τ_{auto} is the duration of the autoacceleration regime and is independent of R_i. Comparison of theory with a number of experimental measurements is presented.

I. Introduction

The Trommsdorff or "gel" effect[1–6] consists of a spectacular increase in conversion rates during the latter stages of free radical polymerization. Hugh increases in molecular weights of the product may be accompanied by rapid temperature rises and even explosive consequences. Both experiment and theory suggest that these effects result from the depression of termination rates due to entanglements, leading to an environment of rapidly increasing polymer concentration and growing entangling power. Termination is further suppressed, chains become even longer, and conversion rates rise still further: the polymerization *autoaccelerates.*

The basic chemistry involved in free radical polymerization, first argued for by Staudinger and collaborators[7,8] in the 1930s, is by now well established. Highly reactive free radical species trigger fast chain reactions which string monomers into polymer chains as follows. When a free radical attacks a monomer, it transfers its active center to the monomer itself, initiating a "live" growing chain, or "macroradical", as successive monomers are added in similar fashion. These living chains propagate into the surrounding monomer medium, with their growth ultimately terminated by interpolymeric reactions in which live pairs annihilate one another's radical end groups. Each termination reaction results in a "dead" chain; this is the final polymer product.

What is needed in order to construct a systematic theory of the phenomenon of autoacceleration? There are three basic processes involved: initiation, propagation, and termination. Of these, the essence of autoacceleration, and the main theoretical difficulty, is undoubtedly the *termination* process which involves complex macromolecular dynamics. The information one requires is the dependence of the polymer–polymer reaction rate constant, k_t, on the chain lengths of a reacting pair and the polymer concentration of the environment. At any instant, the reaction vessel contains a dilute population of growing live chains of various lengths, any two chains amongst which may terminate with one another. Each such reaction occurs in a background of dead polymer chains at a certain concentration ϕ in a solvent of unreacted monomers. In summary, the basic ingredient for a systematic model is the function $k_t(N,M,\phi)$, namely, the dependence of k_t on live chain lengths N and M and inert polymer background volume fraction ϕ (see Figure 1).

A number of theoretical studies of free radical polymerization have incorporated k_t in a systematic fashion. The immediate aim is to predict the dependence of monomer conversion ϕ, namely, the fraction of monomer which has been polymerized, as a function of time and various control parameters. Notice that conversion and dead polymer volume fraction ϕ are directly proportional to one another. Classical experimental conversion profiles $\phi(t)$ are shown in Figures 2–4, exhibiting the characteristic steep growth in polymerization rate as autoacceleration onsets. The simulations of Cardenas and O'Driscoll,[9] in which k_t evolved according to evolving concentration and molecular weights, exhibited Trommsdorff-like effects as entanglements became increasingly important. A significant advance was that of Tulig and Tirrell[10–12] whose model employed termination rate constants based on modern theories of entanglement dynamics[13,14] and was able to demonstrate that autoacceleration derived from heavily suppressed termination. Though these and other models[15] have identified important features of the Trommsdorff effect, a complete physical picture of this complex phenomenon remains elusive, and few analytical theoretical predictions currently exist.

The objective of the present work is to exploit recent theory[16–18] for $k_t(N,M,\phi)$ which allows a relatively "first principles" approach to the polymerization problem. Our aim is a simple theory of autoacceleration from which analytical expressions for conversion rates and other characteristics may be extracted. We treat the simplest

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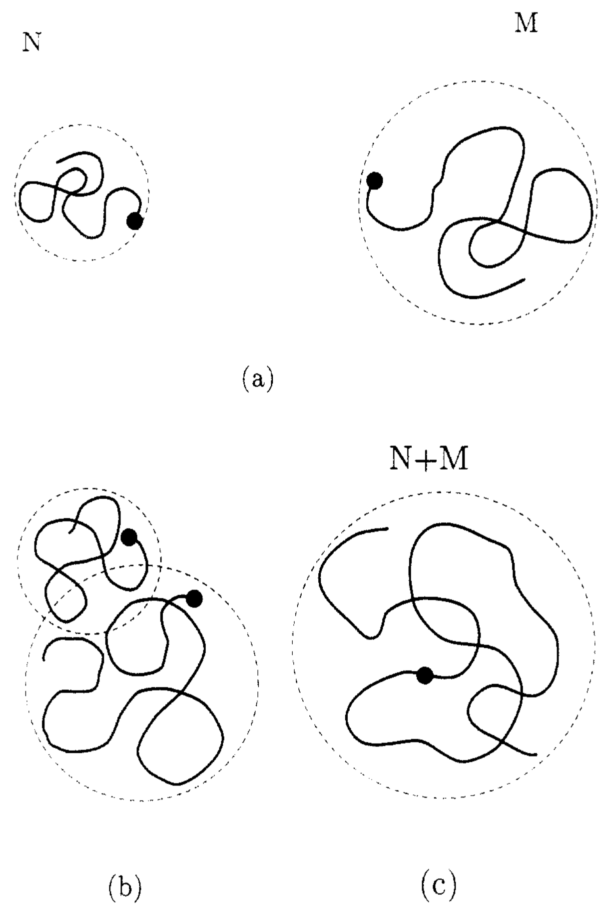

Figure 1. Reactive chains bearing live end groups, which are dilute in an inert polymer background at concentration ϕ (a). When two such live chains of lengths N and M meet through center of gravity diffusion as in b, the number of reactive group collisions during coil–coil overlap governs whether k_t obeys mean-field (MF) or diffusion-controlled (DC) kinetics. If reaction occurs, the end result is a chain of length $N + M$ (c).

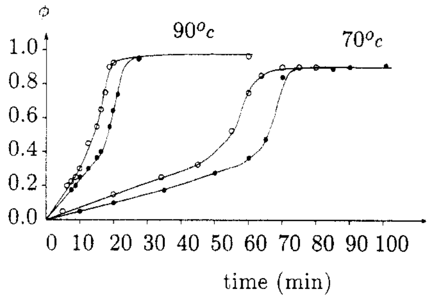

Figure 2. Conversion versus time for bulk polymerization of methyl methacrylate at 70 and 90 °C. Each pair at the same temperature corresponds to a different initial concentration of initiator (AIBN): 0.3 wt % (●) and 0.5 wt % (○). Experimental data from Balke and Hamielec.[33]

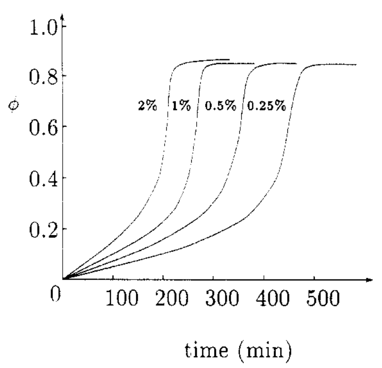

Figure 3. Conversion measurements by Schulz and Harborth[4] of PMMA polymerizations at 50 °C with initiator (benzoyl peroxide) concentration varying from 0.25% to 2%.

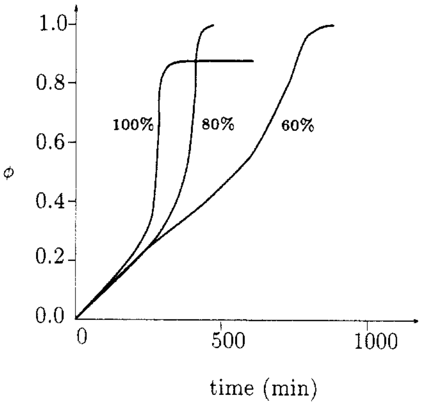

Figure 4. Conversion versus time (Schulz and Harborth[4]) for polymerization of methyl methacrylate at 50 °C in the presence of benzoyl peroxide initiator at various initial concentrations of monomer in benzene.

case, an isothermal bulk polymerization where the polymer–monomer mixture is nonglassy. Part 1 is a study of polymer conversion, while in part 2 we derive explicit forms for molecular weight distributions of the final product. We will use the forms for $k_t(N,M,\phi)$ obtained in ref 18, systematically derived for concentrations from dilute to the melt. The general structure (for $M = N$) is

$$k_t \sim N^{-\alpha}\phi^{-\beta} \tag{1}$$

where the characteristic exponents α and β depend on the relevant concentration regime. We will find in the following sections that, as conversion ϕ increases from the dilute regime to levels sufficiently high that the living chains are strongly entangled in their inert environment, the exponents become so large as to radically change the behavior and induce autoacceleration. Termination rates drop rapidly as ϕ rises, resulting in a growth of the mean living chain length, $\bar{N}$, which in turn both reduces k_t further and increments the rate of polymerization $R_p \propto \bar{N}$. It happens that the magnitudes of α and β are such that the resultant time dependence of ϕ is a very sharp growth.

This is a rather simplified version of events. A crucial effect results from another important property of k_t: the rate constant between two chains is determined by the length of the *smaller* one.[19] As a consequence of this fact, plus the strong decay of k_t with increasing chain length due to entanglements, the total termination rate between all pairs of very long chains turns out to be much less than that between long and short chains, even though the number of chains in the short population, ψ_s, is very small. The characteristic short chain length, z, is defined in terms of an important exponent δ:

$$z \sim \phi^{-\delta} \tag{2}$$

In the simplest case, z is identified with the entanglement threshold, $N_e(\phi)$, in which case "long" ($N \gg z$) translates to "entangled" and "short" ($N \lesssim z$) to "unentangled". This "short-circuit", in which long–long reactions are bypassed in favor of short–long ones, has a profound influence on the effective termination kinetics governing the living population; we will see that kinetics become effectively *first order* in the total number of living chains, ψ_l. Specifically, it will be shown that the total termination rate is

$$R_t \approx k_t(z)\,\psi_s\psi_l \tag{3}$$

in which $k_t(z)$ is the termination rate constant at $N = z$, and the number of short chains scales as the width of the short region of the chain distribution function, $\psi_s \sim z$. But in steady state R_t must match the rate at which new free radicals are generated, R_i. Since R_i is independent of conversion and since the conversion rate is proportional to the number of living chains, one has

$$\dot{\phi} \sim \psi_l \sim \frac{1}{k_t(z)\, z} \sim z^{\alpha-1}\phi^{\beta} \tag{4}$$

which implies an initial growth as

$$\phi \sim t^x, \quad x \equiv [1 + \delta(\alpha - 1) - \beta]^{-1} \tag{5}$$

For actual values of α, β, and δ, the growth exponent x can be very large indeed, and of either sign. When x is negative, the above formula is replaced by a finite-time singularity. In either case, a dramatic autoacceleration is predicted.

The "short–long" termination kinetics of eq 3 lead also to very unexpected dependencies on the initiation rate, R_i. Now we will see later that the number of short chains is simply proportional to the initiation rate. Thus in steady state eq 3 implies that ψ_l, and therefore the polymerization rate, are *independent* of R_i. This is one of our principal predictions. The initiation rate often provides the most important means of controlling the course of a polymerization.

The notion of the importance of two distinct chain populations, short and long, has featured in other theoretical works. Cardenas and O'Driscoll[9] identified z with the entanglement length, employing three constant termination rate constants describing short–short, long–long, and short–long terminations. The ideas which emerge from the present work are very similar in spirit to those of Russell et al. In their studies[15,20,21] z featured as a parameter and it was argued that terminations between short and long chains are dominant, after values $\alpha = 2$ and $\beta = 1$ were postulated for the dependencies of k_t, (eq 1). One should compare this to the exponents $\alpha = 2$ and $\beta = 1.75$ of Tulig and Tirrell.[10] The theory for k_t we will outline in section II leads to somewhat different values.

In the following section general results for $k_t(N,M,\phi)$ are reviewed in brief. We use these forms in section III to attack the polymerization problem in a relatively naive way, employing a simple generalization of the classical Flory theory in which dependence of k_t on chain length and concentration is allowed for. In section IV this scheme is identified as a preaveraging approximation which, though reliable at lower conversions, breaks down after the onset of entanglements. It is necessary to consider the full distribution of living chain lengths, even to infer the mean length. From the kinetic equation governing the distribution, the domination of the termination rate by short–long reactions is demonstrated, and in section V the correct polymerization rate, $\dot{\phi}$, and mean living chain length, $\bar{N}$, are evaluated. Surprisingly, the polymerization rate is independent of the initiation rate. These expressions determine the time evolution of polymer conversion, and in section VI a number of characteristic features are identified. The initial growth is either a strong power or the beginnings of a finite-time singularity, and the approach to full conversion is hyperbolic. Section VII generalizes these results to the case of "weak" systems for which the characteristic short chain scale z is governed by a different exponent δ (see eq 2). Qualitatively, the behavior is unchanged. We conclude in section VIII with a general discussion and a comparison of our results with experimental measurements.

II. Structure of Rate Constant $k_t(N,M,\phi)$

We define the rate constant for the coupling reaction of Figure 1 in terms of the number densities $C(N)$ and $C(M)$ of chains of lengths N and M, respectively:

$$\dot{C}(N) = \dot{C}(M) = -k_t(N,M,\phi)\, C(N)\, C(M) \tag{6}$$

as appropriate[16,22,23] to the situation of dilute live chains N and M in the inert background at concentration ϕ. Note the definition differs slightly from the conventional one (which involves molar densities). In this section and in Appendices A and C, expressions for k_t in the various regimes will be presented after motivation by simplified arguments; the reader is referred to refs 16–18, 24, and 25 for detailed derivations. The main conclusion of these studies is that reaction kinetics in high polymer solutions are either "diffusion-controlled" (DC) or "mean-field" (MF), corresponding to the following forms:

$$k_t \approx DR \approx R^3/\tau \quad (DC), \quad k_t \approx Q_t V P_{eq}^{cont} \quad (MF) \tag{7}$$

Here V is the volume of the reacting vessel, R and τ are respectively the root-mean-square coil size and longest relaxation time, and D is the polymer center of mass diffusivity. Q_t (s^{-1}) is the *local* radical–radical reaction rate (i.e., the reaction probability per unit time *given* that the live radical ends of two growing chains are in contact, i.e., within the chain unit size h of one another) and P_{eq}^{cont} the *equilibrium* radical–radical interchain contact probability.

Whether DC or MF kinetics are applicable depends on the total reaction probability when two reactive coils collide due to center of gravity diffusion.[18] In melts, for example, it turns out that for long enough chains reaction is almost certain during one coil–coil collision (see Figure 1b); in this case, k_t obeys the DC result[16,24,25] of eq 7. Note that this expression has precisely the form of the diffusion-controlled Smoluchowski result[26] for small molecules, except that the "capture radius" (i.e., the reaction range) is replaced by the *coil size* R. This point has been discussed in detail by Doi[24,25] and de Gennes,[16] who showed that in melts the *local* capture radius of the reactive groups is not the appropriate one to appear in the expression for k_t. Instead, because monomers in the melt explore space "compactly" (to use de Gennes' terminology), it is necessary only for the coils to overlap in order that many reactive group collisions be ensured. That is, reaction is guaranteed if the groups approach to within R of each other.

Reaction kinetics are quite different if the reaction probability when two live coils collide is very small. This is the situation which pertains, for example, in dilute solutions in good solvent.[17] In that case, interpolymeric correlations are only weakly removed from equilibrium and the MF form follows.

Note that the short-time monomer diffusion ("segmental diffusion") plays an essential role in the form of reaction kinetics, just as in the "traditional" picture of free radical polymerization termination according to which the segmental diffusion is the rate limiting step.[27] In the theories discussed above, for melts the segmental diffusion (i.e., monomer diffusion during coil–coil overlap) inevitably reacts the active chain units; however, a definite time is required to bring the groups together and thus achieve reaction, namely, τ, which features prominently in the final formula for k_t. In dilute solution the time available, τ, is insufficient for reaction to occur. Thus many coil–coil collisions are required before the segmental diffusion can bring about a reaction event.

At finite polymer concentrations, the class of kinetics is governed by the length N of the reacting chains, as

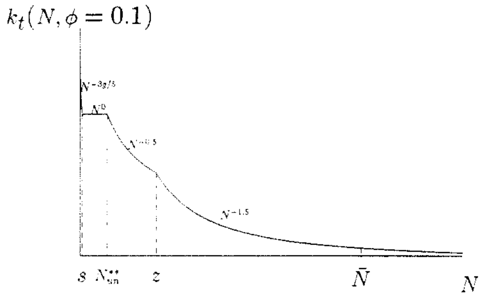

Figure 5. Theoretical k_t (for a "strong" system; see Appendix A) vs number of chain units N, for reacting chains of equal lengths. The background polymer concentration is fixed at $\phi = 0.1$. Four regimes are predicted. For short (i.e., unentangled) regimes k_t decays slowly, $k_t \sim N^{-\alpha}$ with $\alpha < 1$; these are the $N < z$ regimes of eq A2. (For reactive groups at chain ends $g = 0.27$, so $k_t \sim N^{-0.16}$ for $N < s$.) For $N > z$, the decay is strong, $\alpha > 1$. The depicted curve is schematic only; in practice, transitions between regimes are smooth. Values of the crossover scales have been chosen to equal those for PMMA during free radical polymerization at conversion $\phi = 0.1$ (when autoacceleration has barley begun) based on the parameter values used in section V: $s \approx 20$, $N_{un}^{**} \approx 100$, and $z \approx 500$. The mean living chain length $\bar{N} \approx 2000$ at this conversion has also been indicated. For highly reactive end groups, a typical value[34] for k_t at $N = 1$ is $k_t \approx 10^9$ L/mol·s.

described in Appendix A. Chains longer or shorter than a certain characteristic length z obey qualitatively different reaction kinetics. In the simplest case, z is just the entanglement threshold[13,28] whose concentration dependence is determined by the entanglement exponent γ:

$$z = N_e(\phi) \approx N_e^m \phi^{-\gamma} \tag{8}$$

where N_e^m is the melts value. In section IV, z will be identified as the characteristic short chain length discussed in the Introduction, i.e., $\delta = \gamma$ (see eq 2). Experimental values of γ lie in the range[28-32] $1 \lesssim \gamma \lesssim 1.3$.

We will find that autoacceleration is intimately associated with the reaction kinetics of long entangled chains, $N > z$:

$$k_t(N,N,\phi) = k_t(z)\ (z/N)^{3/2} \qquad (N > z) \tag{9}$$

As far as autoacceleration is concerned, the essential feature is the strong decay with increasing chain length, $k_t \sim N^{-3/2}$; the exponent in eq 1 is $\alpha = {}^3/_2$. This is the value obtained by de Gennes for entangled melts,[16] and it arises because kinetics are of the DC type with $R \sim N^{1/2}$ and $\tau \sim N^3$ in the reptation model.[13,14]

In the expression above, we have used $k_t(z)$ to abbreviate the rate constant $k_t(z,z,\phi)$ at the crossover chain length z. This will also feature prominently in our study. One finds (see Appendix A)

$$k_t(z) \approx \frac{Q_t h^3}{\epsilon (N_e^m)^{1/2}} \phi^{\gamma/2-5/8} \tag{10}$$

where ϵ is the dimensionless local radical–radical reaction rate, $\epsilon \equiv Q_t t_h$, and t_h is the monomer relaxation time. A typical value is[6,33] $\epsilon \approx 0.1$. From these expressions it follows that the concentration reaction exponent is identified as $\beta = {}^5/_8 + \gamma$, where $k_t \sim N^{-\alpha}\phi^{-\beta}$.

Reaction kinetics for shorter chains, $N < z$, are qualitatively different. The situation is a little more complex now, with there being several different regimes depending on chain length. These are presented in Appendix A (see eq A2), and the full dependence of k_t on N for fixed ϕ is graphed schematically in Figure 5 for a typical case of PMMA. Each regime has its own values of the exponents α and β. For our purposes, however, the important feature is simply that for all short chains the decay of k_t with chain length is relatively weak. By this we mean that in all short cases α is *less than unity*.

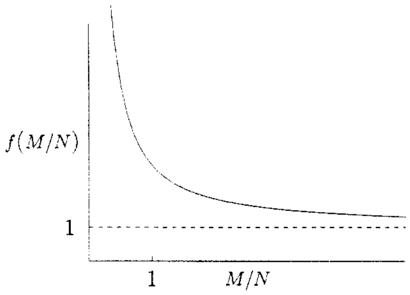

Figure 6. Typical dependence of the scaled dimensionless rate constant $f(M/N) \approx k_t(M,N,\phi)/(Q_t h^3 N^{-\alpha})$ on scaled chain length M/N. Two features are important: for $M/N \gg 1$, f approaches unity ("small wins" property); for $M/N \ll 1$, $f \sim M^{-\alpha}$ diverges either integrably ($\alpha < 1$) or nonintegrably ($\alpha > 1$) depending on the concentration regime.

Now an important feature of the living population is its polydispersity. Thus, it is essential to consider reacting chains of *unequal* lengths, $N \neq M$. Implicitly, we have assumed equal lengths up to this point. The conclusions (see Appendix A) of ref 19 are essentially very simple: kinetics are dominated by the *smallest* chain. The typical behavior is shown in Figure 6; in the limit where one chain is very long, k_t becomes independent of that length. That is, when $N \ll M$, k_t scales as if both chains were of length N:

$$k_t(N) \equiv k_t(N,\infty,\phi) \approx k_t(N,N,\phi) \tag{11}$$

where $k_t(N)$ abbreviates the rate constant between a chain of length N and another chain of much greater length.

These results are theoretical predictions. For discussions of the experimental situation the reader is referred to refs 17, 18, and 34–38. Briefly, the measured concentration dependence of k_t is at least qualitatively in agreement with theory.[39,40] Molecular weight dependence in dilute solution appears to be a very low power,[34] as predicted by eqs A2 and C1, but we are unaware of systematic tests of the high concentration exponent $\alpha = {}^3/_2$. For end groups, there is some experimental support for small chain domination.[36-38]

Let us summarize this section. The chain length z is an important dividing line. Here z has been identified with the entanglement threshold[13,28] N_e. In fact (see ref 18) a second class of reacting polymer solutions exists where z has a slightly different dependence on concentration ϕ. We treat this in section VII. But for either class, the important conclusions are the same:

1. For long chains, $N > z$, k_t decays rapidly due to entanglements: $\alpha > 1$.
2. For short chains, $N < z$, k_t decays slowly: $\alpha < 1$.
3. "Small wins": the rate constant between a pair is determined by the short chain.

III. Flory and Generalized Flory Theory

Having specified the form of termination rate constants, we are now in a position to analyze the polymerizing system. We begin by reviewing the Flory theory,[6] in which chain length dependencies of k_t are neglected. This is certainly inadequate to describe autoacceleration (of which fact Flory was well aware[6]) but is a useful reference point.

For convenience, we will deal with ϕ_i, ϕ_m, and ψ_l, defined to be the volume fractions of initiator, monomer, and macroradicals:

$$\phi_i \equiv h^3[\mathrm{I}], \quad \phi_m \equiv h^3[\mathrm{M}], \quad \psi_l \equiv h^3[\mathrm{M}^\bullet] \qquad (12)$$

where [I], [M], and [M•] are the corresponding number densities. Thus, ψ_l is proportional to the number of living chains per unit volume (ψ_l includes both primary and chain radicals). Since initiator will always be assumed very dilute, $\phi_i \ll 1$, it follows that $\phi_m + \phi \approx 1$. The present study will be restricted to bulk polymerization, $\phi_m \approx 1$ initially, and chain transfer effects[6] will be neglected for simplicity. Our results are thus best compared with polymerizations of species with low transfer constants[6,41] such as poly(methyl methacrylate) (PMMA). This point is discussed further in section VIII. Other than termination rates, the two central quantities are the rate of initiation of free radicals R_i (volume fraction per second) and the chain propagation velocity v_p (chain units per second):

$$R_i = fQ_d\phi_i, \quad v_p = Q_p\phi_m = Q_p(1-\phi) \qquad (13)$$

Here Q_d is the initiator decomposition rate, f the initiation efficiency, and Q_p^{-1} the time to add one unit in a medium of pure monomers.

Before proceeding, a technical point needs clarification. Implicit in eq 12 is the assumption of identical monomer and chain unit volumes, h^3. (The corresponding assumption for initiator is unimportant since the efficiency f can simply be appropriately redefined.) In practice chain monomers (volume v_{pol} are typically[41] smaller than free monomers (v_{mon}), with this of course providing the basis for dilatometry conversion measurements. Now, if one replaces $h^3 \rightarrow v_{pol}, v_{mon}$ as appropriate in eq 12, it is easily shown that eq 15 below is unaffected; i.e., the evolution of $\phi(t)$ is unchanged, as are all other deductions provided one replaces $Q_t \rightarrow Q_t v_{mon}/v_{pol}$. However, by definition conversion is weight fraction, ϕ_w. Thus for experiments in which ϕ_w is measured, one must convert to volume fraction, $\phi = \phi_w/(\phi_w + [1-\phi_w]v_{mon}/v_{pol})$ to compare with our theory for ϕ. The important point is that this translation does not qualitatively change any conclusions of this study. Thus, for convenience we will refer to conversion as ϕ throughout.

Now in the Flory theory[6] k_t is assumed constant, $k_t = Q_th^3$. Hence the total termination rate R_t is given by[6]

$$R_t = Q_t\psi_l^{\,2} \qquad (14)$$

Generally, the steady-state conversion rate $\dot{\phi}$ is determined by the propagation velocity as:[6]

$$\dot{\phi} = v_p\psi_l = R_i\bar{N} \qquad (15)$$

Here $\dot{\phi}$ is equated with the rate at which monomers in the "living system" are converted into monomers in the "dead system". In the Flory theory this is given by $R_i\bar{N}$, where $\bar{N}$ is the mean living chain length, since all macroradical pairs are assumed to terminate with the same termination rate constant regardless of their lengths. The second result in eq 15 then follows from the equality of initiation and termination rates in the steady state (macroradicals are both initiated and terminated in pairs). This leads to

$$\bar{N} = \bar{N}_f \equiv \frac{v_p}{(Q_tR_i)^{1/2}} \qquad (16)$$

Flory theory, though a good approximation at high dilution, worsens as concentration increases; there is clear experimental evidence[27,42–45] that k_t depends on $\bar{N}$ and ϕ even, in fact, at low conversions. The natural generalization is simply to replace $Q_t \rightarrow k_t(\bar{N},\bar{N},\phi)/h^3$ in the above expressions. Looking at eq A2, the $N_{un}^{**} < N < z$ regime is the first candidate for autoacceleration, with the rate constant decaying as $k_t \sim \phi^{-5/8}N^{-1/2}$. Presumably, this leads to a growth in conversion rate. Indeed, on solving eq 16, which now becomes a self-consistent equation for $\bar{N}$, one finds $\bar{N} \sim \phi^{5/12}$ and then eq 15 implies a power law growth of conversion as

$$\phi \sim t^{12/7} \qquad (17)$$

While a faster growth than the linear behavior predicted by Flory theory, experimentally observed autoacceleration is clearly much more dramatic. One looks therefore to the following regime (eq 9), in which entanglements induce an even stronger decay in the rate constant:

$$k_t(\bar{N},\bar{N},\phi) = (Q_th^3/\epsilon)N_e^{m}\bar{N}^{-3/2}\phi^{-(5/8+\gamma)} \qquad (18)$$

Making the replacement $Q_t \rightarrow k_t(\bar{N},\bar{N},\phi)/h^3$ in eq 16 and solving for $\bar{N}$, one has

$$\bar{N} = \bar{N}_{gf} \equiv \left(\frac{\epsilon}{N_e^{m}}\right)^2\bar{N}_f^{\,4}\phi^{5/4+2\gamma} \qquad (19)$$

and eq 15 implies

$$\phi \sim (t_\infty - t)^{-4/(1+8\gamma)} \qquad (20)$$

The assumed constancy of v_p ultimately breaks down of course, as conversion approaches values of order unity (since $v_p \propto \phi_m$), invalidating the result of eq 20 in the latter stages. Nonetheless, a massive rise in conversion rate is predicted. The prediction of this "generalized Flory theory", an approach to a finite-time singularity at t_∞, is spectacular but *wrong*!

IV. Why Generalized Flory Theory Breaks Down

The simple generalized Flory theory correctly identifies entanglements as the cause of autoacceleration but is fundamentally flawed. Its neglect of *molecular weight distribution* leads to a drastic overestimate of the retardation of termination reactions and of $\bar{N}$. The replacement of k_t with its value at the mean living chain length, a preaveraging approximation, while valid for $\bar{N} < z$, in fact breaks down when living chains become highly entangled. This happens at sufficiently high conversions.

A proper treatment must invoke the dynamics of the unnormalized distribution $\psi(N,t)$, defined as the number density of living chains of length N at time t, per unit chain length, multiplied by h^3. Thus, ψ is the volume fraction of radical end groups. The total number of living chains, considered in the previous section, is $\psi_l \equiv \int_0^\infty \psi$. This distribution obeys[42] the following nonlinear and nonlocal kinetic equation:

$$\frac{\partial\psi}{\partial t} = -v_p\frac{\partial\psi}{\partial N} - H\psi, \quad \psi(0,t) = R_i/v_p$$

$$H(N,t) \equiv \frac{1}{h^3}\int_0^\infty \mathrm{d}M\, k_t(N,M)\,\psi(M,t) \qquad (21)$$

where the explicit ϕ-dependence of k_t is dropped for notational ease. On the time scales of eq 21, ϕ is unchanging[6] and may be treated as a fixed parameter.

Dynamics of this type, first proposed by Ito,[42] are the continuous limit of discrete coupled equations more commonly employed. In practice, the values of N involved are very large and the consequent errors negligible. The initial condition follows after identification of $v_p\psi(0,t)$ as the rate of production of chains of "zero" length, i.e., of primary radicals. The termination reaction field, $H(N)$, is the probability per unit time that a given chain of length N terminates with any other macroradical and is determined by the structure of k_t. Note that the "interaction function" between chains N and M, $k_t(N,M)$, is a rather strange one (for example, infinitely different lengths "interact" finitely and a typical chain interacts more strongly with much shorter chains than "nearby" ones).

With the aim of obtaining $\bar{N}$ and ψ_l in steady state, we integrate eq 21 over all N after discarding the time derivative, obtaining

$$R_i = \frac{1}{h^3}\int \mathrm{d}N\,\mathrm{d}M\, k_t(N,M)\,\psi(N)\,\psi(M) \equiv \frac{1}{h^3}\langle k_t(N,M)\rangle_0\, {\psi_l}^2 \qquad (22)$$

The average, $\langle ... \rangle_0$, is with respect to the normalized steady state distribution. The generalized Flory theory amounts to *preaveraging* k_t:

$$\langle k_t(N,M)\rangle_0 \approx k_t(\langle N\rangle_0, \langle M\rangle_0) \equiv k_t(\bar{N},\bar{N}) \qquad (23)$$

whose validity is entirely dependent on the value of the exponent α, $k_t \sim N^{-\alpha}$ (see eq 1). When $\alpha < 1$, the small N and M behavior of k_t in eq 22 is *integrable* and the integral is dominated by the characteristic scale in ψ, namely, $\bar{N}$. Thus one picks up $N, M \approx \bar{N}$, in accord with the preaveraging approximation. Therefore, the analysis for $N < z$ (where $k_t \sim N^{-1/2}$) is essentially valid, and eq 17 captures the correct exponent for the polymerization rate. When $\alpha > 1$, however, the procedure is wrong. This is most clearly reflected in the steady-state reaction field $H(N)$ of eq 21 for large values of N; since $\psi(0)$ is fixed by the boundary condition, and ψ can be shown to be monotonically decreasing, the integral is *dominated by small M*:

$$H(N) = \frac{1}{h^3}\int_0^\infty \mathrm{d}M\, k_t(M)\,\psi(M) \equiv H_s \qquad (N \gg n^*) \qquad (24)$$

The fact that the rate constant for a pair of reacting polymers is dominated by the *smallest* chain plays a crucial role. Thus for entangled chains $N, M \gg z$ in the integrand of eq 21, one has $k_t(N,M) \sim M^{-3/2}$ whenever $M < N$ (see eqs 9 and 11). This divergence is qualitatively different from that characterizing the unentangled regimes, being so strong as to be *unintegrable* at the origin; integrated against a well-behaved function, the effective cutoff $M = z$ dominates (for short chain scales, $M < z$, k_t crosses over to integrable form, i.e., $\alpha < 1$). Provided N is sufficiently large, the function $k_t(N,M)$ can be replaced by its infinite N limit

$$k_t(M) \equiv k_t(M,\infty,\phi) \qquad (25)$$

This replacement is permissible for M values up to order N. But since $\int_0^N \mathrm{d}M\, k_t(M)\,\psi(M)$ converges for upper limit large compared to z, then provided N is sufficiently large the upper limit can be replaced by ∞ and one obtains the result of eq 24. The corrections due to the contributions from $M > N$, which are evaluated in Appendix B, are small provided N is greater than a certain scale n^* which will be derived below.

Equation 24 is a remarkable result. The reaction field acting on long chains is a *constant*, which we have named H_s. This conclusion depends only on the most general properties of the rate constant k_t: for long (short) chains k_t is unintegrable (integrable) at the origin.

What reaction field acts on shorter chains, $N < n^*$? In this case it turns out that H is dominated by longer chains, $M > N$. Looking at eq 21, the contribution from such M values is roughly $h^{-3}k_t(N)\int_N^\infty \psi$ (using the small wins principle again). For small enough N, this integral is negligibly different to the total normalization of ψ and one obtains

$$H(N) = \frac{1}{h^3}k_t(N)\,\psi_l \qquad (N \ll n^*) \qquad (26)$$

In deriving the above results we have assumed that the mean chain length is much greater than the characteristic short chain length, $\bar{N} \gg z$. We will see (self-consistently) that when conversion is sufficiently high this is indeed true. It implies that the *great majority of living chains are long*. Therefore, to within small errors of order $z/\bar{N}$, the total number of macroradicals ψ_l and the number of long macroradicals are one and the same.

The expressions for the reaction field above have a very clear physical interpretation. Equation 26 states that the field acting on a short chain of length N is essentially due to the long chains in the living system. There are ψ_l such long chains. Since almost all of these are bigger than N, the relevant rate constant according to the small wins principle is in every case $k_t(N)$. This leads to the displayed result. Physically, a short chain almost certainly terminates with a long one.

This domination of the total termination rate by short–long events is also apparent from the long chain field expression, H_s of eq 24. Recalling that the integral is dominated by $M \approx z$, we can estimate its value as

$$H_s \approx k_t(z)\,\psi_s \qquad (27)$$

where the number of short chains is approximately given by

$$\psi_s \approx z\psi(z) \qquad (28)$$

Thus, the field acting on long chains (i.e., on almost all chains) is dominated by the short population, $N \lesssim z$, whose characteristic length is z.

From these expressions, it is simple to determine the crossover length n^* where the long and short forms of the field H coincide. Using $\psi(z) \approx \psi_l/\bar{N}$ (which follows because ψ has width $\bar{N}$ and $\psi(z)$ is of order $\psi(0)$ when $z \ll \bar{N}$), one obtains

$$n^*/z \approx (\bar{N}/z)^{2/3} \qquad (29)$$

implying that $z \ll n^* \ll \bar{N}$. That is, n^* is a scale respectively much greater and much smaller than the characteristic short chain and long chain scales, and it follows that almost all living chains are longer than n^* and experience the long chain field H_s. In Appendix B the leading corrections to H_s are shown to be of order $(n^*/N)^{3/2}$, while corrections to the short chain ($N \ll n^*$) result of eq 26 are of order $(N/n^*)^{3/2}$ or $N/\bar{N}$ for the cases $N > z$ and $N < z$, respectively.

It is now clear why generalized Flory theory breaks down. It assumes a "uniform" reaction field $H \approx h^{-3}k_t(\bar{N},\bar{N})\psi_l$ which is dominated by the typical chain length $\bar{N}$. This at first sight appears reasonable since most chains have a length of order $\bar{N}$. But when entanglements onset, $k_t \sim N^{-3/2}$ decays so rapidly that the total rate of termination of a given long chain with all other long chains is very small, even though most other chains are long. That is, the motions of long chains are so restricted by entanglements that they are unlikely to react with one another.

Instead, the reaction field they experience is dominated by the *smallest* members of the living population, $M \lesssim z$. A long living chain is far more likely to terminate with a small chain than any other.

The main conclusions of this section on the autoacceleration regime are as follows:

1. The chain length n^* is the natural dividing line between short chains (characteristic length z) and long chains (characteristic length $\bar{N}$): $z \ll n^* \ll \bar{N}$.
2. The reaction field acting on long chains is a constant, $H = H_s$. This result is *exact* in the limit $\bar{N}/z \to \infty$.
3. The field on short chains is $H(N) = h^{-3}k_t(N)\psi_l$, exact in the same limit.
4. During autoacceleration almost all living chains are long. Therefore, almost all chains experience a *constant* reaction field.

V. Calculation of $\bar{N}$ and Polymerization Rate $\dot{\phi}$

In this section, the expressions for the reaction field H acting on short and long chains (eqs 24 and 26, respectively) will be used to calculate mean lengths and net termination rates of the living chains. The rates at which short and long chains terminate are respectively given by

$$R_t^{\text{short}} \equiv \int_0^{n^*} H\psi, \quad R_t^{\text{long}} \equiv \int_{n^*}^{\infty} H\psi \tag{30}$$

Integrating the living dynamics of eq 21 in steady state and using the short and long forms of H, one finds

$$R_t^{\text{short}} = H_s\psi_l = \upsilon_p[\psi(0) - \psi(n^*)]$$

$$R_t^{\text{long}} = H_s\psi_l = \upsilon_p\psi(n^*) \tag{31}$$

These results are exact for $\bar{N}/z \to \infty$, with errors of order $n^*/\bar{N}$. The equality $R_t^{\text{short}} = R_t^{\text{long}}$ is a direct consequence of short–long domination; each termination event involves one short and one long living chain. Indeed, we can now verify the short–long dynamics asserted in the introduction (eq 3): the total termination rate $R_t \equiv \int_0^\infty H\psi$ is given by $R_t = 2H_s\psi_l \approx k_t(z)\ \psi_s\psi_l$ after making use of eq 27.

Equation 31 implies an interesting property of the steady-state living chain distribution,

$$\psi(n^*) = \psi(0)/2 \tag{32}$$

This states that from the moment of birth until growing to a length n^*, a macroradical has a termination probability equal to exactly $^1/_2$; since short and long chains terminate at equal rates, being terminated in pairs, the total termination probability of a growing chain while short must equal the total termination probability while long.

Another expression for the living distribution at the short–long dividing line n^* follows from the steady-state solution to eq 21, namely, $\psi(n^*) = \psi(0)\ e^{-\int_0^{n^*} H/\upsilon_p}$. Using the short chain form for H, one finds the integral converges for upper limit of order z. Hence, since $n^* \gg z$, one obtains

$$\psi(n^*) = \psi(0)\ \exp\{-(h^3\upsilon_p)^{-1}\psi_l\int_0^\infty dN\, k_t(N)\} \tag{33}$$

with errors of order $n^*/\bar{N}$. These two expressions for $\psi(n^*)$ imply the following result for the polymerization rate $R_p \equiv \dot{\phi}$:

$$\dot{\phi} = \upsilon_p\psi_l = \frac{\upsilon_p^{\,2}\, h^3 \ln 2}{\int_0^\infty k_t} \tag{34}$$

This is one of the principal results of the present study. The rate of conversion is *independent* of the initiation rate R_i, a very different prediction to the famous result of the classical Flory theory, $R_p \sim R_i^{1/2}$.

The second objective of this section is the mean living chain length $\bar{N}$, whose value follows immediately from the main conclusion of section IV: long chains experience a constant reaction field H_s. From eq 21 in steady state this implies an exponential, or "Flory", distribution for most of the living population:

$$\psi(N \gg n^*) = \psi(n^*)\ e^{-H_s\upsilon_p^{-1}(N-n^*)} \approx \frac{\psi(0)}{2}e^{-N/\bar{N}}, \qquad \bar{N} = \upsilon_p/H_s \tag{35}$$

This distribution has normalization $\psi(0)\ \bar{N}/2$ which can be equated to the total normalization ψ_l with small error since almost all chains are long. Remembering the boundary condition on the living dynamics, $\psi(0) = R_i/\upsilon_p$, this leads to

$$\bar{N} = \frac{\upsilon_p^{\,2}h^3\ 2\ln 2}{R_i\int_0^\infty k_t} \tag{36}$$

The mean living length (the "kinetic" chain length) varies inversely with initiation rate R_i. Again, this is very different from the classical prediction $\bar{N} \sim R_i^{-1/2}$.

This expression for $\bar{N}$ is exact in the limit of very long living chains. From it, one can approximate its dependence on conversion by using $\int_0^\infty k_t \approx zk_t(z)$ and recalling that the propagation rate is proportional to the monomer concentration (eq 13). Then, using eq 8 and eq 10 for z and $k_t(z)$, respectively, one finds

$$\bar{N} \approx \frac{\epsilon}{N_e^{m\,1/2}}\bar{N}_f^{\,2}\phi^y\ (1-\phi)^2 \tag{37}$$

where $y \equiv {}^5/_8 + \gamma/2 \approx 1.1$ for a typical value of the entanglement exponent $\gamma \approx 1$. The Flory result $\bar{N}_f$ has been taken at low conversion (i.e., $\upsilon_p \to Q_p$ in eq 16). For a typical system, such as PMMA at about 100 °C, one has[10,28,33] $\gamma \approx 1$, $N_e^m \approx 50$, $\bar{N}_f \approx 10^3$, and[18] $\epsilon \approx 0.1$. At a conversion $\phi = 0.5$, this gives $\bar{N}/\bar{N}_f \approx 5$ which is close to experimental values. The relationship between $\bar{N}$ and our previous, incorrect, generalized Flory attempt is immediately obtained from eqs 19 and 8: $\bar{N} = (z\bar{N}_{gf})^{1/2}$. This implies that $\bar{N} \ll \bar{N}_{gf}$ when the polymerizing system is well into the autoacceleration regime, i.e., when $\bar{N} \gg z$. This is not a surprising discovery since the short–long domination, which invalidated the generalized Flory result, only served to increase termination rates and reduce living chain lengths.

To establish the conversion ϕ_{onset} at which autoacceleration begins, one sets $\bar{N} = n^* = z$ using the result in eq (37). Thus

$$\phi_{\text{onset}} = \left(\frac{(N_e^m)^{3/4}}{\sqrt{\epsilon}\bar{N}_f}\right)^{4/(3\gamma+5/4)}, \quad \frac{\bar{N}}{n^*} = \left(\frac{\phi}{\phi_{\text{onset}}}\right)^{(12\gamma+5)/24} \tag{38}$$

which gives $\phi_{\text{onset}} \approx 0.06$ and $\bar{N}/n^* \approx (\phi/\phi_{\text{onset}})^{0.7}$ for the values used above to estimate $\bar{N}$. The ratio $\bar{N}/n^*$ measures "distance" into the autoaccelerating regime. Thus, provided $\phi \gg \phi_{\text{onset}}$, one of the assumptions upon which our reasoning has relied, namely, $\bar{N} \gg n^* \gg z$, is justified. That is, the calculated mean living molecular weight is highly entangled. Notice that all four scales z, $\bar{N}_{gf}$, n^*, and $\bar{N}$ are degenerate at onset.

To conclude this section, we remark that, by establishing the simple exponential form for the distribution of long living chains (eq 35), we have also established the self-consistency of the arguments presented here. These have assumed that for long chains ψ is a well-behaved function with width much greater than z.

VI. Time Dependence of Conversion: Autoacceleration

Our starting point is obtained from eqs 34 and 36 which imply

$$\dot{\phi} = R_i \bar{N}/2 \qquad (39)$$

a different relationship to that of Flory theory, $\dot{\phi} = R_i \bar{N}$. The factor of $^1/_2$ results from two facts: (1) each short–long termination produces a dead chain of length almost exactly equal to that of the long member of the terminating pair, and (2) such termination events occur with rate constant independent of the long chain length (small wins).

Using this relation, one can then obtain the dependence of $\dot{\phi}$ on ϕ through eq 37, which expresses $\bar{N}$ in terms of ϕ. This leads to

$$\dot{\phi} = \frac{1}{\tau_{\text{auto}}} \phi^{\gamma/2+5/8} (1-\phi)^2, \quad \tau_{\text{auto}} \equiv \frac{(N_e^m)^{1/2}}{\epsilon} \frac{Q_t}{{Q_p}^2} \qquad (40)$$

The time scale τ_{auto} is the duration of the strongly autoaccelerating behavior. Consider first low conversions where the $(1-\phi)^2$ factor is relatively unimportant. Then the time dependence is of two possible types depending on the magnitude of γ. For smaller values, a strong power law growth follows:

$$\phi \approx (t/\tau_{\text{auto}})^x, \quad x \equiv 8/(3-4\gamma) \qquad (\gamma < 3/4) \qquad (41)$$

but for typical values $\gamma \approx 1$ the characteristic exponent x changes sign, and a growth more rapid than any power or exponential is predicted:

$$\phi \approx \left(\frac{t_\infty - t}{\tau_{\text{auto}}}\right)^{-|x|} \qquad (\gamma > 3/4) \qquad (42)$$

This is a finite-time singularity at a scale t_∞ (whose precise value depends on the duration of earlier regimes), with a characteristic power governing the approach to the divergence. For example, with $\gamma = 1$ one would have $\phi \sim (\Delta t)^{-8}$ where $\Delta t \equiv t_\infty - t$.

These time dependencies describe the initial behavior only, of course; the above growth laws cannot run their full course and in reality are checked either by the onset of the glass transition of the reacting polymer solution or by monomer exhaustion. The present study is confined to the latter route. To encompass the full evolution, therefore, one must account for the reduction in monomer propagation velocity as full conversion is approached; i.e., the $(1-\phi)^2$ factor in eq 40 must be included. A typical trajectory defined by this equation, with $\gamma = 1$, is graphed in Figure 7. The distinctive and experimentally relevant features are the strong initial growth and the final asymptote to full conversion whose characteristic exponent is easily extracted from eq 40. In these latter stages, one has $\dot{\overline{1-\phi}} \approx -(1-\phi)^2/\tau_{\text{auto}}$ whence

$$1 - \phi \approx \left(\frac{t}{\tau_{\text{auto}}}\right)^{-1} \qquad (t > \tau_{\text{auto}}) \qquad (43)$$

This hyperbolic approach to completion is a rather specific prediction of our theory and is a direct consequence of the quadratic dependence of $\bar{N}$ on v_p (see eq 36). We predict a behavior quite different from that implied by naive applications of either Flory theory ($\bar{N}_f \propto v_p$, giving exponential approach) or generalized Flory theory ($\bar{N}_{gf} \propto v_p^4$, giving $1 - \phi \sim t^{-1/3}$).

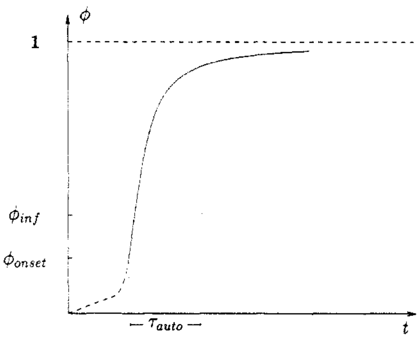

Figure 7. Theoretical conversion versus time for autoacceleration above the glass transition temperature for a weak system. τ_{auto} is the duration of the regime (see eqs 40 and 47 for strong and weak systems, respectively). A sharp initial growth onsets at ϕ_{onset}, and the final asymptote is hyperbolic, $1 - \phi \approx \tau_{\text{auto}}/t$. An inflexion point occurs at $\phi = \phi_{\text{inf}}$. The dashed curve represents the typical low conversion behavior preceding autoacceleration.

In practice one expects that at conversions of order unity the semidilute power laws,[13] which were assumed to derive the exponent y of eq 37, will become unreliable (see section VIII for a discussion of this point). Thus, while the final approach (eq 43) is predicted to be universal, at intermediate ϕ the trajectory described by eq 40 is probably best viewed as merely a guide to the realized behavior. If we nonetheless interpret it literally, the complete trajectory of $\phi(t)$ is then predicted to be the same for all systems provided time is measured in units of τ_{auto}. A characteristic feature of the transition region connecting the initial growth to the final asymptote is the inflexion point ($d^2\phi/dt^2 = 0$), at which the value of ϕ is determined only by the exponent γ: $\phi_{\text{inf}} = (4\gamma + 5)/(4\gamma + 21)$, or $\phi_{\text{inf}} \approx 0.36$ for $\gamma \approx 1$.

VII. Weak Systems

In the preceding sections, the onset of autoaccelerating behavior has been identified with the moment at which the living chains first become entangled, i.e., when $\bar{N} = z = N_e$ where N_e is the entanglement threshold. This is the characteristic of "strongly reacting" systems. At this point, k_t develops a stronger dependence on chain length, $\alpha > 1$. This results from the fact that the reaction kinetics are of DC type and the chain dynamics are simultaneously entanglement-dominated.[18]

Now in ref 18 it is demonstrated that entanglements may in fact onset *before* these kinetics first apply. Such systems are labeled "weakly reacting" since at $\bar{N} = N_e$ their kinetics still belong to the weak MF regime; N must grow to even larger values before DC behavior onsets and α first attains a value larger than unity (see Appendix C). That is, the value of z is different for weak systems.

In this section we treat these weak cases. There are no changes in the essential behavior. Since k_t has the same basic structure, i.e., unintegrable (integrable) for $N > z$ ($N < z$), the fundamental results, eqs 34 and 36, are unchanged. The long chain reaction kinetics remain $k_t = k_t(z)(z/N)^{3/2}$, which implies that the expressions for n^* are also no different.

The only differences lie in the dependencies of z and $k_t(z)$ on concentration and other parameters[18] (see Appendix C):

$$z \approx \left(\frac{N_e^m}{\epsilon}\right)^{2/3} \phi^{-(8\gamma+6g+5)/12}, \quad k_t(z) \approx Q_t h^3 \phi^{3g/4} \text{ (weak)} \qquad (44)$$

where the "correlation hole" exponent[13,46–48] $g \approx 0.27$. These expressions lead to slightly different power laws for $\bar{N}$ and

ϕ. Beginning with $\bar{N}$, the basic result of eq 36 now leads to

$$\bar{N} \approx \left(\frac{\epsilon}{N_{\rm e}^{\rm m}}\right)^{2/3} \bar{N}_{\rm f}^{2} \phi^{y} (1-\phi)^2 \text{ (weak)} \tag{45}$$

where the exponent is now $y = (8\gamma - 3g + 5)/12$. Thus, roughly, $\bar{N} \sim \phi(1-\phi)^2$ for $\gamma = 1$, $g \approx {}^1/_4$ which is a slightly weaker conversion dependence than $\bar{N} \sim \phi^{1.1}(1-\phi)^2$ for the same parameters in the strong case (eq 37). Using the parameter values quoted directly after eq 37, one estimates $\bar{N}/\bar{N}_{\rm f} \approx 7$. From eq 45 it is easily verified that the relationship between $\bar{N}$, z, and $\bar{N}_{\rm gf}$ is unaltered. Setting $\bar{N} = z$, the onset conversion $\phi_{\rm onset}$ and the distance into the autoaccelerating regime are now given by

$$\phi_{\rm onset} \approx \left\{\left(\frac{N_{\rm e}^{\rm m}}{\epsilon}\right)^{2/3} \frac{1}{\bar{N}_{\rm f}}\right\}^{24/(16\gamma+3g+10)},$$
$$\frac{\bar{N}}{n^*} = \left(\frac{\phi}{\phi_{\rm onset}}\right)^{(16\gamma+3g+10)/36} \text{ (weak)} \tag{46}$$

which leads to $\phi_{\rm onset} \approx 0.05$ and $\bar{N}/n^* \approx (\phi/\phi_{\rm onset})^{0.7}$. These are values similar to those for strong systems.

The above expression for $\bar{N}$ leads to conversion dynamics

$$\dot{\phi} = \frac{1}{\tau_{\rm auto}} \phi^{(8\gamma-3g+5)/12} (1-\phi)^2, \quad \tau_{\rm auto} = \left(\frac{N_{\rm e}^{\rm m}}{\epsilon}\right)^{2/3} \frac{Q_{\rm t}}{{Q_{\rm p}}^2} \text{ (weak)} \tag{47}$$

which exhibits the same qualitative behavior as that for the strong case. The early growth is again a strong power or a finite-time singularity depending on γ:

$$\phi \approx \begin{cases} (t/\tau_{\rm auto})^{x}, & \gamma < \gamma_{\rm c} \equiv (3g + 7/8) \\ (\Delta t/\tau_{\rm auto})^{-|x|}, & \gamma > \gamma_{\rm c} \end{cases} \tag{48}$$

where $\Delta t \equiv t_\infty - t$ is the distance from the singularity and the exponent x depends very sensitively on γ: $x = 12/(-8\gamma+3g+7)$. If $\gamma = 1$, for example, the "singularity" behavior is predicted, with $x \approx -50$! This is a consequence of the fact that $\gamma_{\rm c}$ is very close to unity.

Finally, the approach to full conversion is essentially unchanged, $1 - \phi \sim 1/t$, with the $(1-\phi)^2$ factor in eq 47 being independent of the weak or strong quality. The detailed trajectory is slightly different, however, with the conversion at the inflexion point now equal to $\phi_{\rm inf} = (8\gamma - 3g + 5)/(8\gamma - 3g + 29)$. For $\gamma = 1$, this gives a value which is almost identical to that in the strong case.

VIII. Conclusions

This work has identified the onset of the Trommsdorff effect with a concentration-induced transition in termination kinetics. Beyond this point, kinetics are both diffusion-controlled and entanglement-dominated. The outstanding features of these kinetics are as follows: (i) the reaction rate between two polymers of very different lengths is determined entirely by the *small* chain; (ii) the domination of the small chain is determined by a power α ($k_{\rm t} \sim N^{-\alpha}$) which *exceeds unity.* Feature (ii) implies that, quite generally, if one sums reaction rates between a chain of a certain length and a family of shorter chains, the sum is dominated by the shortest members of that family. This would not be the case if (i) were true but (ii) were untrue. The consequence on termination reactions is dramatic: the net rate of termination in the autoacceleration regime turns out to be almost exclusively due to short–long reactions. This idea, that short–long events can dominate termination even though the short population is much smaller than the long one, has also been an important feature of the work of Russell et al.[15,20,21]

The two main results of this work are eqs 34 and 36, for the polymerization rate and mean living chain length:

$$\dot{\phi} = \frac{{v_{\rm p}}^2 h^3 \ln 2}{\int_0^\infty k_t}, \quad \bar{N} = \frac{{v_{\rm p}}^2 h^3\, 2 \ln 2}{R_{\rm i} \int_0^\infty k_t} \tag{49}$$

We claim these are *exact* in the limit of very large $\bar{N}$. They are very robust, since they depend only on very general features of the rate constant $k_{\rm t}$: all that is required is that the large N behavior of $k_{\rm t}$ be unintegrable at the origin and that $k_{\rm t}$ be dominated by the smaller chain of a pair. The particular form, power law or otherwise, is unimportant provided the unintegrable property holds. Thus, for example, these conclusions do not rely on the power law which emerges from a reptation theory framework, $k_{\rm t} \sim N^{-3/2}$. Provided the integral of $k_{\rm t}$ converges rapidly at large N, our two basic results remain valid. They imply very different dependencies to those of the classical Flory theory: $\dot{\phi}$ is independent of $R_{\rm i}$ and $\bar{N} \sim 1/R_{\rm i}$. These are predicted to be *universal* features of autoacceleration.

These universal aspects should be compared with the more tentative predictions concerning the time dependence of ϕ and the conversion dependence of $\bar{N}$ (e.g., eqs 37 and 41). These are extrapolations of the two basic results and rely on semidilute power laws whose validity is questionable at conversions of order unity. Thus, while the trend indicated by these laws is expected to be realistic, i.e., sharp growths in ϕ and $\bar{N}$, the precise exponents involved are less so. However, two features of the time dependence are claimed to be universal. First, the duration of the autoacceleration regime $\tau_{\rm auto}$ is predicted independent of $R_{\rm i}$ (see eqs 40 and 47). This follows generally from the fundamental result for $\dot{\phi}$. Second, the long time behavior $1 - \phi \sim 1/t$ was a consequence of $\dot{\phi} \sim (1-\phi)^2$, which in turn follows from the general relation $\dot{\phi} \sim {v_{\rm p}}^2$ in eq 49. Thus, hyperbolic decay of monomer concentration during the closing stages is predicted to be universally true for nonglassy polymerizations, up until the point when $\bar{N}$ becomes so small that living chains are no longer strongly entangled.

Our main experimental predictions, then, are that both the slope of $\phi(t)$ and the width of its autoacceleration region are independent of initiator species and concentration, at a given ϕ value and temperature. Figure 2 exhibits conversions as a function of time, measured by Balke and Hamielec for bulk PMMA polymerization at different temperatures and AIBN initiator concentrations. Their experiments were performed at 50, 70, and 90 °C, all of which are below the melt glass transition temperature $T_{\rm g} \approx 114$ °C. Our theory should therefore be compared with these experiments only at conversions somewhat lower than the final glassy plateaus and at higher temperatures. The two higher temperatures are plotted in Figure 2; each pair corresponds to initiator concentrations (proportional to $R_{\rm i}$) in the ratio 3:5. At 90 °C, the curves are very close to being parallel (inasmuch as one can judge from the available data) in the domain $0.5 \lesssim \phi \lesssim 0.8$ where our model should apply, and the widths are apparently about equal. At this temperature, the data indicate that autoacceleration begins close to $\phi \approx 0.4$–0.5 which, in view of eq 38 and our estimate $\phi_{\rm onset} \approx 0.06$, would suggest that $\bar{N}/n^* \approx 4$ is required before the entanglement-induced short–long effect takes over. This is physically reasonable. Note that $\phi_{\rm onset}$ is in general highly species-dependent, being determined by all of the relevant microscopic parameters, namely, $Q_{\rm d}$, $Q_{\rm p}$, $Q_{\rm t}$, $t_{\rm h}$, and $N_{\rm e}^{\rm m}$. For polystyrene, for example, $\phi_{\rm onset}$ is very large,[49] and $R_{\rm i}$ dependence close to that predicted by the Flory theory persists until rather high conversions. Returning to the data of Figure 2, up to $\phi \approx 0.4$ the roughly linear form, which extrapolates to the origin and whose slope is clearly different for different R_i, is strongly suggestive of preautoacceleration regimes where the Flory theory (then a fairly good approximation) implies[6] $\dot{\phi} \propto (R_i)^{1/2}$. A crude comparison of the slopes of the two regions gives $\bar{N}/\bar{N}_f \approx 4$ which accords with our estimate following eq 37.

A second set of PMMA conversion measurements are shown in Figure 3, those of Schulz and Harborth.[4] In the relevant very steep domains, $0.5 \lesssim \phi \lesssim 0.8$, though changes of slope by factors of order unity are difficult to judge accurately, the slopes appear to exhibit a small decrease with decreasing R_i at a rate which is less than that implied by the $(R_i)^{1/2}$ Flory result.

Now since[6] low conversion measurements indicate that Q_t/Q_p^2 is generally a decreasing function of temperature, from eqs 40 and 47 it is reasonable to anticipate that τ_{auto} will follow the same trend since ϵ and N_e^m are expected to be relatively weak functions of temperature. The data of Figure 2 and that of Sack et al.[50] are both consistent with this trend. Using Q_t/Q_p^2 values compiled in ref 10 leads to estimates $\tau_{auto} \approx 250$ and 150 s for the 70 and 90 °C curves, respectively, of Figure 2 (using the weak result (eq 47) and the same ϵ and N_e^m estimates as previously used). These values are close to experiment for 90 °C but about $^1/_4$ of the duration at the lower temperature. A similar estimate for the PMMA experiments of Sack et al.[50] agrees well with the measured values, $\tau_{auto} \approx 10^4$ s.

A frequently discussed feature is the relation between ϕ_{onset} and the mean molecular weight at that point.[34] In our model, the exponent a governing this relationship is identified with $1/\delta$ (eq 2)

$$\phi_{onset}(\bar{N}_{onset})^a = \text{const.}, \quad a = \delta^{-1} \tag{50}$$

since $\bar{N}$ and z are degenerate at onset (see eqs 38 and 46). This gives $a = 1/\gamma \approx 1$ and $a \approx 0.8$ (using $\gamma = 1$ in eq 44) for the strong and weak cases, respectively. Experimental values[11,34,51–55] in the range $0.24 \lesssim a \lesssim 1.0$ are quoted; however, we emphasize that our definition is based on the *living* $\bar{N}$ which in part 2 is shown to equal, essentially, the mean *instantaneous* dead chain length. We do *not* expect a simple correlation between ϕ_{onset} and the mean cumulative dead chain length $\bar{N}^{cum}$, since the latter is the result of a series of earlier regimes physically unrelated to autoacceleration. Reported experimental values are frequently based on $\bar{N}^{cum}$.

The data of Figure 4 include polymerizations whose final route to completion is monomer exhaustion rather than the onset of glassiness. These are measurements of $\phi(t)$ for PMMA solution polymerizations at 50 °C in benzene solvent at various initial dilutions as indicated. Our work here has dealt with bulk polymerization; however, many qualitative features will remain unchanged in the presence of solvent. The 60% and 80% curves are clearly above T_g for these dilutions at final complete conversion, while the bulk curve is clearly below (complete conversion is never attained). The final asymptote for the glassy case is much sharper than those for the nonglassy cases; the more rounded finishes for the latter are at least qualitatively consistent with our hyperbolic prediction. Further experiment, exploring completion in $T > T_g$ polymerizations, would be very interesting in this respect.

Let us now consider some assumptions which have led to the results of this paper. Implicit in the use of a long-time rate constant $k_t(N,M,\phi)$ is a picture of nonoverlapping living chains whose growth rates are much less than their intrinsic relaxation times. To check the validity of this picture, we compare the lifetime of a growing chain, i.e., the radical lifetime $\tau_{rad} \approx \bar{N}/\upsilon_p$, with the longest relaxation time of both long and short chains, namely

$$T_{long} \approx \left(\frac{\bar{N}}{N_e^m}\right)^3 \left(\frac{N_e^m}{s}\right)^2 t_h, \quad T_{short} \approx z^2 t_h \tag{51}$$

where the long result is the reptation time[13,14,18] and T_{short} the Rouse time.[13,14] The latter is appropriate to strong systems but also provides a close estimate in the weak case. The scale s is defined in Appendix A. For the above PMMA system one finds $T_{short}/\tau_{rad} \approx 10^{-4}$ and $T_{long}/\tau_{rad} \approx 0.1$ (using values $Q_p \approx 10^4$ and $t_h = \epsilon/Q_t \approx 10^{-9}$ s). Thus, long–long reactions are adequately treated in our picture, though quite near to the limit. Most importantly, the use of asymptotic expressions for k_t describing short–long pairs is completely vindicated, since one can show that the validity of these expressions requires that time scales be large compared to the short chain relaxation time, rather than that of the long chain. Short–long events are of course the crucial events in our picture. We have also estimated the "overlap parameter" for living chains,[13] finding it to be roughly 0.1 for long and only 10^{-5} for small.

The conclusion is that our coil–coil reaction picture is realistic for sufficiently high temperatures (or, equivalently, sufficiently low conversions). However, the estimate just made for T_{long} is sensible only sufficiently far above T_g. For example, PMMA melt viscosities increase by as much as 5 orders of magnitude from 120 to 20 °C above T_g, while PMMA self-diffusivities ($N \approx 200$) in melts of longer PMMA chains at 20 °C above T_g are[56] as low as 10^{-17} cm^2/s. This implies a relaxation time of order $T_{long} \approx 10^4$ s, which is so great that other mechanisms will take over, such as the "residual termination" considered by Russell et al.[57] in which radicals meet by the propagation mechanism itself. However, our detailed conclusions require only that T_{short} be smaller than τ_{rad}; this will remain true up to higher conversions since small molecule diffusion is observed[58] to remain at relatively large values even very close to T_g. When even short chain mobility is significantly reduced, our general conclusions (eq 49) are robust, as discussed, but the function $k_t(N)$ will be a different object altogether.

It has been assumed that the only feature of the dead background chains which enters k_t is their concentration ϕ. Is it justified to ignore their mean length and length distribution? Provided they are not too short, theory suggests that the answer is yes: in the reptation picture,[13] the chains comprising the entangled environment of a given reptating chain of length N must be much smaller, $\lesssim N^{1/3}$, before nonreptation processes provide faster relaxation mechanisms. Thus the long chain form ($N > z$) of k_t is unaffected provided autoacceleration is well-developed, since there are very few dead chains of length $\lesssim \bar{N}^{1/3}$. This implies that the basic results (eq 49) are insensitive to details of the background. However, one expects these details to influence the precise numerical value of short chain scales at a given concentration, e.g., the short–long dividing scale z.

Another central assumption has been that the living population reaches steady state long before the conversion ϕ can change substantially. That is, $\tau_{rad} \ll \tau_{auto}$ has been assumed. This assumption underlies the result $R_i = R_t$, and one can demonstrate this to be justified for typical systems. For instance, for the PMMA system discussed here, one finds $\tau_{rad} = \bar{N}/\upsilon_p$ is on the order of several seconds at the height of autoacceleration. This is much less than the time scale on which ϕ changes, with τ_{auto} being on the order of several hundred seconds (see, for example, Figure 2).

To compare with the predictions of this work, experimental polymerizations should be conducted isothermally as far as is possible, this having been assumed by the theory. Deviations from isothermal conditions have been documented experimentally.[59] If temperature increases, rate constants will change; for instance, the propagation velocity v_p will presumably increase and $\bar{N}$ become greater than under isothermal conditions. Spatial temperature variations will also influence conversion rates and molecular weights. These are interesting and complex issues beyond the scope of the present study.

Finally, chain transfer[6] effects (in which the live radical at the end of a growing chain is transferred to a monomer, initiator molecule, or dead polymer) have been neglected. For PMMA,[41] transfer constants to the monomer, $C_M \equiv Q_{tr,m}/Q_p$ where $Q_{tr,m}$ is the local transfer rate constant, are small. At 60 °C, for example, $C_M \approx 10^{-5}$ is estimated, and with $\bar{N} \approx 10^4$ transfer would then be a small effect (since $\bar{N}C_M$ represents the number of transfer events in the lifetime of a living chain). Nonetheless, chain transfer may be the origin of the slight decrease in conversion rate with decreasing R_i which is apparent from the PMMA data of Figure 3. For other species, C_M can be substantial. For instance,[6] for vinyl chloride $C_M \approx 10^{-3}$ at 60 °C, while for vinyl acetate $C_M \approx 10^{-4}$ at the same temperature. Generally, it is important to realize that chain transfer effects influence not only molecular weight distributions but also conversion rates since k_t depends on N. Only in Flory theory is this dependence neglected. These issues will be treated elsewhere.

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Appendix A. Rate Constant $k_t(N,M,\phi)$ for "Strong" Systems

In ref 18 it is argued that a given reacting polymer solution may be one of two types: "strongly" or "weakly" reacting. This appendix deals with the "strong" case, treated in sections II–VI, where the crossover scale z is the entanglement threshold. Generally, z is defined as the chain length above which the reaction exponent $\alpha > 1$, where $k_t \sim N^{-\alpha}$. This happens when chains are long enough to be simultaneously strongly entangled and to obey DC reaction kinetics.[18]

The key quantity is the *mean number of collisions* $\mathcal{N}^{\text{coll}}$ between the radical end groups of each chain during the duration, τ, of one coil–coil collision:

$$\mathcal{N}^{\text{coll}} \approx \frac{\tau}{t_h} P_{\text{eq}}^{\text{cont}} \frac{V}{R^3} \tag{A1}$$

This is the conditional radical–radical contact probability *given* coil–coil overlap, multiplied by the number of time intervals (t_h being the local chain unit relaxation time). DC kinetics apply if $\mathcal{N}^{\text{coll}} \gg 1$, since reaction is then certain should two reactive coils overlap. If $\mathcal{N}^{\text{coll}} \ll 1$, reaction is unlikely during such an encounter and MF kinetics prevail. (In refs 60 and 61, MF kinetics were referred to as a generalized "law of mass action" (LMA) whose conventional form equates reaction rates to the equilibrium contact probabilities of small molecules.)

Consider a solution at concentration ϕ, well above the overlap threshold, where the solvent is a good one. This is the case most relevant to free radical polymerizations, where the monomer usually acts as a good solvent for polymers of its own type.[62] Now if R is much less than the screening length[13,14] $\xi \approx hs^{3/5}$, i.e., if $N \ll s$ where $s \approx \phi^{-5/4}$ is the number of monomers per "blob" of size ξ, then the reacting chains behave as in dilute solution.[13] Thus[13] $\tau \sim R^3$ and[13,14,63] $P_{\text{eq}}^{\text{cont}} \sim N^{-3g/5}$, where g is des Cloizeaux's "correlation hole" exponent,[46–48] $g \approx 0.27$. It follows that $\mathcal{N}^{\text{coll}} \sim N^{-3g/5}$ becomes very small for long chains, leading to MF kinetics, $k_t \sim N^{-3g/5}$.

The screening of excluded volume between larger chains, $N > s$, results in a considerable enhancement of contact probabilities. A similar argument leads to $k_t \sim P_{\text{eq}}^{\text{cont}} \sim s^{-3g/5}$; that is, in the dilutelike result one simply replaces N with s.

Now inspection of eq A1 reveals that $\mathcal{N}^{\text{coll}}$ is actually an *increasing function* of N when $N > s$. For example, if the reacting chains are unentangled, their dynamics are Rouse-like and $\mathcal{N}^{\text{coll}} \sim N^{1/2}$, since $R \sim N^{1/2}$ and $\tau \sim N^2$. Eventually, therefore, MF kinetics must *cross over* to the DC form for large enough N, $k_t \sim N^{-1/2}$, using eq 7. Thus

$$k_t(N,N,\phi) \approx \begin{cases} Q_t h^3 N^{-3g/5} & (N < s) \\ Q_t h^3 s^{-3g/5} & (s < N < N_{\text{un}}^{**}) \\ k_t(z)\ (z/N)^{1/2} & (N_{\text{un}}^{**} < N < z \equiv N_e) \end{cases} \qquad \text{(strong)} \tag{A2}$$

Note that for all of the above "short" regimes, the reaction exponent α of eq 1 is *less than unity*. The crossover chain length N_{un}^{**} is obtained[18] from eq A1 by equating the total reaction probability, namely, $Q_t t_h \mathcal{N}^{\text{coll}}$, to unity. Expressing the quantities therein in terms of ϕ, one readily obtains $N_{\text{un}}^{**} \approx (Q_t t_h)^{-2} \phi^{-(5+6g)/4}$. From eq A2 one can then derive the expression for $k_t(z)$ displayed in eq 10 in the main text.

For entangled chains, $N > z$, reptation theory predicts[13,14] $\tau \sim N^3$, and the Rouse DC form of eq A2 crosses over to the "long" chain expression eq 9 whose outstanding feature is $\alpha > 1$. In Figure 5 the full N-dependence is shown for a strong system, at fixed conversion $\phi = 0.1$.

Implicitly, equal chain lengths $N = M$ have been assumed in deriving eqs A2 and 9. For the general case, these equations remain valid provided N is interpreted as the length of the shorter of the two chains. More precisely, it is demonstrated in ref 19 that

$$k_t(N,M,\phi) = k_t(N) f\left(\frac{M}{N}\right), \quad f(u) = \begin{cases} 1, & u \gg 1 \\ u^{-\alpha}, & u \ll 1 \end{cases} \tag{A3}$$

where $k_t(N) \equiv k_t(N,\infty,\phi) \sim N^{-\alpha}$, and the details of the crossover function f are regime-dependent. A typical form is shown in Figure 6. When N is much smaller than M (the situation of most interest in this study) f is close to unity.

Appendix B. Corrections to Asymptotic Results for Reaction Field $H(N)$

Using the "small wins" rule, H in eq 21 can be approximately written as

$$h^3 H \approx \int_0^N \mathrm{d}M\, k_t(M)\, \psi(M) + \int_N^\infty \mathrm{d}M\, k_t(N)\, \psi(M) \tag{B1}$$

With a view to estimating corrections to the large N result of eq 24, we write this as

$$H \approx H_s\{1 + \int_N^\infty \mathrm{d}M\, [k_t(N) - k_t(M)]\, \psi(M)/H_s\} \tag{B2}$$

Since k_t is monotonic decreasing, the correction term is bounded by $k_t(N) \int_N^\infty \psi / H_s$. Then, since $\int_N^\infty \psi \approx \bar{N}\psi(N)$, and using eqs 27 and 29, one finds

$$H = H_s\{1 + O(n^*/N)^{3/2}\} \qquad (N \gg n^*) \tag{B3}$$

In a similar fashion, one can easily show that the relative correction to the short chain field of eq 26 is approximately given by

$$H(N \ll n^*) = k_t(N)\,\psi_1\{1 + \int_0^N \mathrm{d}M\, k_t(M)\,\psi(M)/k_t(N)\,\psi_1\} \tag{B4}$$

Now when $z \ll N \ll n^*$, the integral in the numerator of the correction term is dominated by $M \approx z$ and gives approximately $zk_t(z)\,\psi(z)$. With $\psi(z) \approx \psi_1/\bar{N}$, this leads to

$$H(z \ll N \ll n^*) = k_t(N)\,\psi_1\{1 + O(N/n^*)^{3/2}\} \tag{B5}$$

When N is much less than z the same integral is dominated by its upper limit since in the $M < z$ domain exponents α are less than unity for all regimes. Thus

$$H(N \ll z) = k_t(N)\,\psi_1\{1 + O(N/\bar{N})\} \tag{B6}$$

Appendix C. Rate Constant k_t for "Weak" Systems

For the weak case, there are just two "short chain" regimes. These are in fact identical to the two shortest regimes in the strong case, shown in eq A2. But, by definition of "weakly reactive",[18] as N increases at fixed ϕ the second of these two regimes persists even after the onset of entanglements. A direct transition to the final "entangled DC kinetics" regime subsequently occurs. The criterion for this MF → DC transition is based on reptation (not Rouse) dynamics, for which[18] the reaction probability, $Q_t t_h \mathcal{N}^{\mathrm{coll}} \approx \epsilon N^{3/2}/N_e(\phi)\ s^{1/2+3g/5}$, is again an increasing function of N which approaches unity at a threshold $N \approx N_{\mathrm{ent}}^{**}$:

$$k_t(N,N,\phi) \approx \begin{cases} Q_t h^3 N^{-3g/5} & (N < s) \\ Q_t h^3 s^{-3g/5} & (s < N < z \equiv N_{\mathrm{ent}}^{**}) \end{cases} \qquad \text{(weak)} \tag{C1}$$

The expression for $z = N_{\mathrm{ent}}^{**}$ is given in eq 44. The rate constant at $N = z$ is just the constant "semidilute MF" expression, $k_t(z) \sim s^{-3g/4}$, shown also in eq 44. For $N > z$, the form in eq 9 is applicable just as for strong systems, albeit with the redefined z and $k_t(z)$.

References and Notes

(1) Norrish, R. G. W.; Brookman, E. F. *Proc. R. Soc. London, A* **1939**, *171*, 147.
(2) Norrish, R. G. W.; Smith, R. R. *Nature (London)* **1942**, *150*, 336.
(3) Schulz, G. V.; Blaschke, F. *Z. Physik. Chem.* **1941**, *B50*, 305.
(4) Schulz, G. V.; Harborth, G. *Makromol. Chem.* **1947**, *1*, 106.
(5) Trommsdorff, E.; Kohle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1*, 169.
(6) Flory, P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1971.
(7) Staudinger, H.; Brunner, M.; Frey, K.; Garbsch, P.; Signer, R.; Wehrli, S. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 241.
(8) Staudinger, H.; Kohlschutter, H. W. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2019.
(9) Cardenas, J.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 883.
(10) Tulig, T. J.; Tirrell, M. *Macromolecules* **1981**, *14*, 1501.
(11) Tulig, T. J.; Tirrell, M. *Macromolecules* **1982**, *15*, 459.
(12) Tirrell, M.; Hanley, B.; Balloge, S.; Tulig, T. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*, 299.
(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1985.
(14) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1986.
(15) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 9.
(16) de Gennes, P.-G. *J. Chem. Phys.* **1982**, *76*, 3316, 3322.
(17) Friedman, B.; O'Shaughnessy, B. *Macromolecules* **1993**, *26*, 5726.
(18) O'Shaughnessy, B. *Phys. Rev. Lett.* **1993**, *71*, 3331.
(19) O'Shaughnessy, B. Submitted to *Makromol. Chem., Rapid Commun.*
(20) Adams, M. E.; Russell, G. T.; Casey, B. S.; Gilbert, G.; Napper, D. H.; Sangster, D. F. *Macromolecules* **1990**, *23*, 4624.
(21) Maxwell, I. A.; Russell, G. T. *Makromol. Chem., Theory Simul.* **1993**, *2*, 95.
(22) Peliti, L. *J. Phys. A* **1986**, *19*, L365.
(23) Friedman, B.; Levine, G.; O'Shaughnessy, B. *Phys. Rev. A* **1992**, *46*, R7343.
(24) Doi, M. *Chem. Phys.* **1975**, *11*, 107.
(25) Doi, M. *Chem. Phys.* **1975**, *11*, 115.
(26) von Smoluchowski, M. *Z. Phys. Chem.* **1917**, *92*, 192.
(27) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
(28) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley and Sons: New York, 1980.
(29) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.
(30) Klein, J. *Macromolecules* **1978**, *11*, 852.
(31) Richards, W. D.; Prud'homme, R. K. *J. Appl. Polym. Sci.* **1986**, *31*, 763.
(32) Tirrell, M. *Rubber Chem. Technol.* **1986**, *57*, 523.
(33) Balke, S. T.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1973**, *17*, 905.
(34) Mita, I.; Horie, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1987**, *C27* (1), 91.
(35) Gebert, M. S.; Torkelson, J. M. *Polymer* **1990**, *31*, 2402.
(36) Gebert, M. S.; Yu, D. H. S.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 4160.
(37) Yu, D. H.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 852.
(38) Horie, K.; Schnabel, W.; Mita, I.; Ushiki, H. *Macromolecules* **1981**, *14*, 1422.
(39) Mita, I.; Horie, K.; Takeda, M. *Macromolecules* **1981**, *14*, 1428.
(40) Gebert, M. S.; Torkelson, J. M. *Polymer* **1990**, *31*, 2402.
(41) Odian, G. *Principles of Polymerization*; John Wiley and Sons: New York, 1981.
(42) Ito, K. *J. Polym. Sci.* **1974**, *12*, 1991.
(43) O'Driscoll, K. F.; Mahabadi, H. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 869.
(44) Mahabadi, H.-K. *Macromolecules* **1985**, *18*, 1319.
(45) Mahabadi, H.-K. *Macromolecules* **1991**, *24*, 606.
(46) des Cloizeaux, J. *J. Phys. (Paris)* **1980**, *41*, 223.
(47) Schafer, L.; Vonferber, C.; Lehr, U.; Duplantier, B. *Nuclear Physics B* **1992**, *374*, 473.
(48) Duplantier, B. *J. Stat. Phys.* **1989**, *54*, 581.
(49) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1345.
(50) Sack, R.; Schulz, G. V.; Meyerhoff, G. *Macromolecules* **1988**, *21*, 3345.
(51) Turner, D. T. *Macromolecules* **1977**, *10*, 221.
(52) Lee, H. B.; Turner, D. T. *Macromolecules* **1977**, *10*, 226.
(53) Lee, H. B.; Turner, D. T. *Macromolecules* **1977**, *10*, 231.
(54) Lee, H. B.; Turner, D. T. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1977**, *18*, 539.
(55) O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2159.
(56) Green, P. F.; Russell, T. P.; Jerome, R.; Granville, M. *Macromolecules* **1989**, *22*, 908.
(57) Russell, G. T.; Napper, D. H.; Gilbert, G. *Macromolecules* **1988**, *21*, 2133.
(58) Horie, K.; Mita, I.; Kambe, E. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2663.
(59) Zhu, S.; Hamielec, A. E. *Polymer* **1991**, *32*, 3021.
(60) Friedman, B.; O'Shaughnessy, B. *Macromolecules* **1993**, *26*, 4888.
(61) Friedman, B.; O'Shaughnessy, B. *Europhys. Lett.* **1993**, *23*, 667.
(62) Grulke, E. A. Solubility Parameters: In *Polymer Handbook*, 3rd ed.: Brandrup, J.; Immergut, E., Eds.; John Wiley and Sons: New York, 1989.
(63) Witten, T. A.; Prentis, J. J. *J. Chem. Phys.* **1982**, *77*, 4247.