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Autoacceleration in Free Radical Polymerization. 2. Molecular Weight Distributions

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ABSTRACT: Molecular weight distributions during autoacceleration in free radical polymerization are calculated within the framework developed in part 1. Most macroradicals (living chains) are so immobilized by entanglements that they terminate with short mobile unentangled chains with rate constants independent of their own lengths. In some respects, Flory's "equal reactivity" hypothesis is recovered, leading to a Flory (exponential) distribution of the living population for most chain lengths N. The instantaneous distribution of the polymer product, $\dot{\psi}_d$, is a copy of the living one. Its mean length is $\bar{N}_d \sim 1/R_i$ where R_i is the initiation rate. For the shortest chains, $\dot{\psi}_d$ exhibits power law behavior with exponents determined by short chain termination kinetics and vanishes at $N = 0$. It follows that $\dot{\psi}_d$ is peaked at $N = z$, the characteristic short chain length.

I. Introduction

In part 1 of this study,[1] a simple theory of the Trommsdorff or "gel" effect[2–4] in bulk free radical polymerization was developed. Expressions were obtained for polymerization rates, whose "autoacceleration" is the signature of the Trommsdorff effect, and for mean molecular weights of the growing macroradical population, the so-called living chains. In this paper molecular weight distributions will be calculated, beginning with the living population. The living distribution will then be used to calculate that of the final polymer product, the dead chains.

It was found in part 1 that autoacceleration is associated with entanglement-dominated termination reaction kinetics. The evolution of the conversion ϕ (the fraction of monomer polymerized) is governed by the structure of the rate constant $k_t(N,M,\phi)$ for terminations between living pairs of lengths N and M. These occur in an environment of dead polymer chains at concentration ϕ which eventually becomes so high that most living chains are entangled. Rates of reaction are then so strongly suppressed that typical long entangled living chains terminate not with each other but instead with much shorter unentangled ones. There are very few such short chains, but they nonetheless provide the fastest available mechanism. The dominant role of "short–long" terminations leads to rates of polymerization $\dot{\phi}$ and mean living lengths $\bar{N}$ which are very different from those of the classical Flory theory.[4] It was shown, in particular, that $\dot{\phi}$ is *independent* of the rate of free radical initiation R_i, while $\bar{N} \sim 1/R_i$.

Here we will extend the analysis to molecular weight distributions (MWDs). Of interest are both the cumulative dead MWD, namely, the distribution of all chains which have been produced up to the present moment, and, of much clearer physical origin, the "instantaneous" dead MWD. This lettter, the time derivative of the cumulative, is the distribution of dead chains which are being produced at some instant by termination of living chains. It is by far the most natural quantity to study theoretically and is the main object of this work. We remark that throughout this paper we will always deal with *number* rather than weight distributions.

To obtain the distribution of dead chains, one needs first the living MWD about which we have already established a great deal in paper 1. There it was found that the long entangled living chains (which comprise almost all of the living population) are distributed exponentially; i.e., they follow a "Flory" distribution. The principal conclusion of the present paper is that for long chains the dead MWD is a *copy* of the living MWD.

This may appear a strange result at the very conversions where the basic assumption of Flory theory,[4] namely, the constancy of k_t, is most strongly violated. The explanation lies in the short–long picture. Now an important feature of reaction kinetics between polymers of very different lengths is that k_t is determined by the smallest of a reacting pair.[5] But a long living chain is most likely to terminate with a short one, the rate constant for which will therefore be independent of the long chain length. One thus recovers, in some sense, the conditions of equal macroradical reactivity which lead to the Flory distribution. This will be discussed in detail later.

Let us mention some relevant experimental results. Cumulative MWD measurements by Balke and Hamielec[6] are reproduced in Figure 1 at several conversion values. A trend to much broader distributions at larger ϕ values is clear; this is the result of autoacceleration. The bimodal shape at larger ϕ is a superposition of low and high conversion distributions. However, quantitative conclusions are difficult since the axes are highly nonlinear functions of chain length N. Measurements by Sack et al.[7] of mean (number-average) cumulative dead chain lengths, $\bar{N}_d^{\mathrm{cum}}$, are presented in Figure 2. These were used by the authors to infer (dashed line) the instantaneous average $\bar{N}_d$ which grows as autoacceleration onsets and then peaks. These data should be viewed relative to the time dependence of conversion for the same polymerization, which is shown in Figure 3. Amongst the few theoretical works which have aimed to predict these features of MWDs are those of Cardenas and O'Driscoll[8,9] who numerically solved equations determining the dead cumulative MWD after dividing the living population into short and long chains. In agreement with experiment, the distribution was found to develop bimodal features at high conversions.

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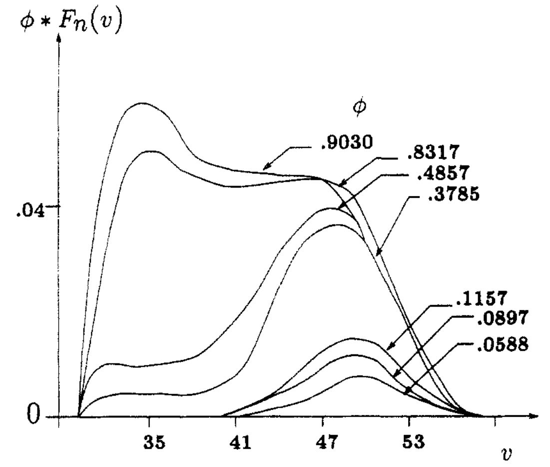

Figure 1. Cumulative GPC results of Balke and Hamielec[6] for bulk PMMA radical polymerization at 70 °C (initial concentration of AIBN initiator, 0.3 wt %) at various conversions as indicated. Raw chromatogram heights $F(V)$ are shown versus retention volume V which decreases nonlinearly with increasing molecular weight. Areas under the $F(V)$ curve are proportional to the total weight of the polymer.

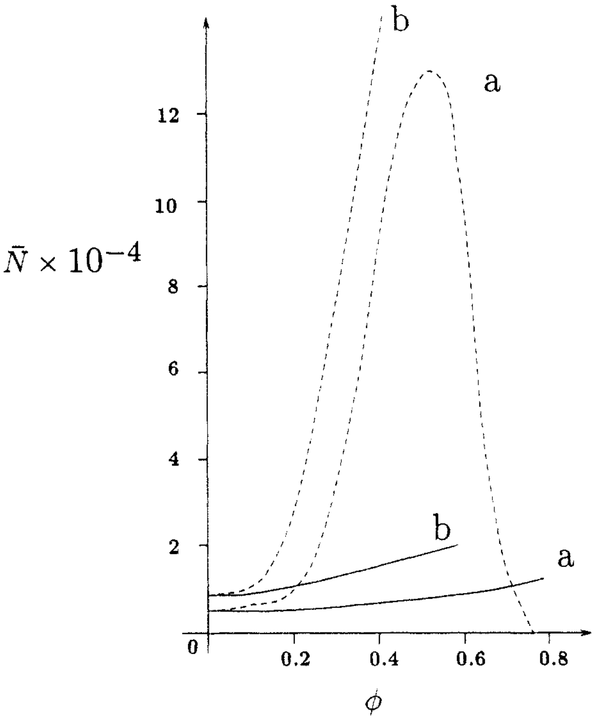

Figure 2. Number-average degrees of polymerization (PMMA, ACN initiator, 0 °C) versus conversion ϕ, as measured by Sack et al.[7] (see Figure 3 for conversion profiles). Initiator concentrations are (a) 6.4×10^{-3} and (b) 1.6×10^{-3} mol L^{-1}. The solid and dashed lines denote cumulative ($\bar{N}_d^{cum}$) and instantaneous ($\bar{N}_d$) averages, respectively.

Before detailed calculation, let us quantify the preceding remarks concerning the rate constant. The "small wins" property[5] is described by a crossover function f whose most important feature is $f(\infty) = 1$:

$$k_t(N,M,\phi) = k_t(N)\, f(M/N), \quad k_t(N) \equiv k_t(N,\infty,\phi) \tag{1}$$

Here we use the abbreviation $k_t(N)$ for the rate constant between a chain of length N and another of much greater length. The big chain length drops out completely. According to the theory of ref 10, its general structure is $k_t(N) \sim N^{-\alpha}\phi^{-\beta}$ where the exponents α and β vary from one concentration regime to another. The crucial feature of reaction kinetics for the long entangled chains[10,11] is

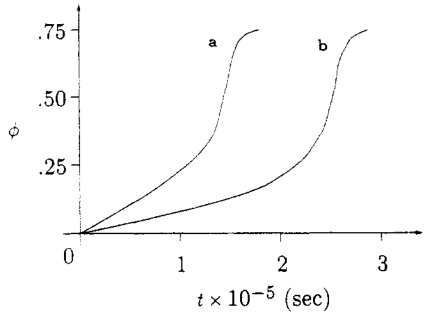

Figure 3. Conversion versus time for the PMMA polymerizations of Figure 2 by Sack et al.[7] a and b correspond to a and b of figure 2.

that the exponent α exceeds unity

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

The divergence at small N is unintegrable. This feature leads to short–long domination; when integrated, the dominant contribution is from short chains of characteristic length z. Chains shorter than z obey radically different kinetics whose length exponent α is less than unity; k_t is then integrable at the origin. The specific forms for short chains are presented in Appendix A.

The different values of α above and below $N = z$ mean that summation over a range of N values in the short region produces a very different result to a summation in the long region. For example, $\int_{N_1}^{N_2} k_t$ is dominated by its upper limit if $N_1, N_2 \ll z$, and by its lower limit if $N_1, N_2 \gg z$. In the former case the largest chain lengths dominate and in the latter case the smallest. It also follows that, if one integrates *through* z, the scale z itself dominates. For example:

$$\int_0^\infty \mathrm{d}M\, k_t(M) \approx z k_t(z) \tag{3}$$

Precisely defined, chains longer than z obey reaction kinetics which are diffusion-controlled and dominated by entanglements[1,10] (these have the property $\alpha > 1$). In the simplest case, z is then identified with the entanglement threshold N_e, but it may happen that z is a longer scale than N_e. These two possibilities were labeled respectively "strongly" and "weakly" reacting systems in ref 10. Their respective kinetics and expressions for z are presented in Appendix A. However, the differences for our purposes are not very important; the most significant property of the short scale $z \sim \phi^{-\delta}$ is simply that it decreases as conversion proceeds, according to the exponent δ. At sufficiently high conversion it becomes much less than the characteristic length of "long" chains, namely, $\bar{N}$. Then the fraction of chains which are short, of order $z/\bar{N}$, is very small; during autoacceleration almost all chains are long. The onset of autoacceleration is identified with the conversion at which $\bar{N}$ and z first become equal.

The structure of this paper is as follows. In section II living MWDs will be calculated. The instantaneous dead distribution is deduced in section III by summing termination events between all possible living pairs which produce a dead chain of a given length, weighted with termination rate constants appropriate to the pairs involved. For long chains, the result is that the living MWD is simply copied into the dead. Short chains follow power law distributions determined by the short chain forms of k_t described in Appendix A. All results are discussed and physically motivated in section IV.

II. Living Molecular Weight Distribution

We define the living distribution $\psi(N,t)$ to be the number density of living chains of length N at time t, per unit chain length, multiplied by the volume of one monomer unit, h^3. Thus, ψ is the volume fraction of radical end groups attached to living chains. Note that this distribution is unnormalized. In part 1 ψ was studied according to nonlinear and nonlocal dynamics[1,12] whose steady-state form is

$$v_{\mathrm{p}} \frac{\partial \psi}{\partial N} = -H\psi, \quad \psi(0) = R_{\mathrm{i}}/v_{\mathrm{p}}$$

$$H(N) \equiv \frac{1}{h^3}\int_0^\infty \mathrm{d}M\, k_{\mathrm{t}}(N,M,\phi)\, \psi(M) \tag{4}$$

in which v_{p} is the propagation velocity, i.e, the number of monomers per second added to a growing living chain. This relation simply equates the steady-state propagation current to that due to termination. The latter is determined by $H(N)$, the termination reaction field, namely, the probability per unit time that a macroradical of length N terminates with any other. We will deal exclusively with steady-state quantities in the following.

In part 1 it was shown that during autoacceleration H assumes rather simple forms for large and small N:

$$H(N \ll n^*) = h^{-3} k_{\mathrm{t}}(N)\, \psi_{\mathrm{l}}, \quad H(N \gg n^*) = h^{-3}\int_0^\infty \mathrm{d}M\, k_{\mathrm{t}}(M)\, \psi(M) \equiv H_{\mathrm{s}} \tag{5}$$

where $n^* \approx z(\bar{N}/z)^{2/3}$ is the natural dividing line between short ($N \lesssim z$) and long ($N \approx \bar{N}$) chains and $\psi_{\mathrm{l}} \equiv \int_0^\infty \psi$ is the total number of macroradicals. These asymptotic forms reflect short–long domination: long chains experience a reaction field which is dominated by small chains and thus, due to the "small wins" principle, is a constant, H_{s}; meanwhile, the small N field is dominated by long chains of which there are approximately ψ_{l} since almost all chains are long. Since each termination event involves a short–long pair, it follows that the total termination probability of a growing macroradical while short must equal that while long. Correspondingly, it was found that

$$\psi(n^*) = \psi(0)/2 \tag{6}$$

The constant reaction field H_{s} experienced by long chains tells us that they follow a Flory distribution:

$$\psi(N \gg n^*) = \frac{\psi(0)}{2}\mathrm{e}^{-N/\bar{N}}, \quad \bar{N} = \frac{{v_{\mathrm{p}}}^2 h^3 2 \ln 2}{R_{\mathrm{i}}\int_0^\infty \mathrm{d}N\, k_{\mathrm{t}}(N)} \tag{7}$$

as derived in part 1. This is the MWD describing most of the living population. Using the small N form of the reaction field, the steady-state solution to eq 4 for shorter chains is given by

$$\psi(N \ll n^*) = \psi(0) \exp\left\{\frac{-\ln 2\int_0^N k_{\mathrm{t}}}{\int_0^\infty k_{\mathrm{t}}}\right\} \tag{8}$$

where use was made of eq 6 and the fact that the integral of k_{t} converges for upper limit greater than but of order z. This result, as eq 7, is exact in the limit $\bar{N}/z \to \infty$.

The explicit forms for the short living MWD are obtained by inserting the appropriate expressions for k_{t} as given in Appendix A. However, some general features are immediately apparent when we recall that the length exponent α is less than unity for all short regimes. Thus $\int_0^N k_{\mathrm{t}} \sim N^{1-\alpha}$ increases with N and ψ decreases accordingly throughout the $N < z$ regime. But since we know that ψ drops to $\psi(0)/2$ for a value of N somewhat greater than z, it follows that

$$\psi(N) \approx \psi(0) \qquad (N \ll z) \tag{9}$$

Thus, the living MWD is essentially equal to its value at $N = 0$ (namely, $R_{\mathrm{i}}/v_{\mathrm{p}}$) throughout the two shortest regimes for strongly reacting systems ($N < N_{\mathrm{un}}^{**}$ in eq A1) and throughout the first regime for weakly reacting systems ($N < s$ in eq A2). The only issue is how ψ varies in the regimes immediately preceding z. Now since $\psi(z)/\psi(0)$ is of order unity and since $k_{\mathrm{t}} \sim N^{-\alpha}$ with $\alpha < 1$, one has

$$\psi \approx \psi(0) \exp\{-(N/z)^{1-\alpha}\} = \begin{cases} \psi(0) \exp(-(N/z)^{1/2}) & N_{\mathrm{un}}^{**} < N < z \text{ (strong)} \\ \psi(0) \exp(-N/z) & s < N < z \text{ (weak)} \end{cases} \tag{10}$$

where the values $\alpha = {}^1/_2$ and 0 were used for the strong and weak cases, respectively (see eqs A1 and A2).

The remaining living lengths to consider are those between the typical short scale z and the short–long dividing scale n^*. For these, k_{t} has already reached its long chain form $k_{\mathrm{t}} \sim N^{-3/2}$ and it is clear from the general solution in eq 8 that, when $N > z$, the living distribution will be very close to its value at n^*, namely, $\psi(0)/2$. Using eq 3, one finds

$$\psi \approx \frac{\psi(0)}{2}\mathrm{e}^{(z/N)^{1/2}} \qquad (z < N < n^*) \tag{11}$$

This is a plateaulike approach to the value at n^*.

To summarize this section, the living MWD is essentially a Flory distribution for all chains longer than z, since the plateau region is in practice probably indistinguishable from the early stages of the broad exponential decay. Short chains comprise a small fraction of the total population, and the characteristic short chain length z is much less than the mean length $\bar{N}$. In this very narrow region, ψ drops by a factor of 2. The approach to z from lower N values is either a stretched exponential (with exponent ${}^1/_2$) or a pure exponential.

III. Instantaneous Dead Molecular Weight Distribution

The living distribution determines the rate at which dead polymers of length N are being produced at some instant:

$$\dot{\psi}_{\mathrm{d}}(N) = \frac{1}{2h^3}\int_0^N \mathrm{d}M\, k_{\mathrm{t}}(N-M,M)\psi(N-M)\psi(M) \tag{12}$$

This is the instantaneous distribution. It is the time derivative of $\psi_{\mathrm{d}}(N,t)$, the total number of chains of length N, per unit chain length, produced by the time t. Since each termination event annihilates a pair of radicals, the normalization of $\dot{\psi}_{\mathrm{d}}$ is half of the total rate at which living chains terminate, $R_{\mathrm{t}}/2$, which in steady state must equal $R_{\mathrm{i}}/2$. One can easily verify this with the help of eq 4.

A great simplification arises for long chains, $N \gg z$. Consider the contribution in that case from small M, $M \ll N$, for which the integrand in eq 12 approximates $k_{\mathrm{t}}(M)$ $\psi(N)\, \psi(M)$ after applying the "small wins" rule to k_{t}. Now, since $\int_0^N k_{\mathrm{t}}(M)\, \psi(M)$ converges for upper limit of order z, when $N \gg z$ one can replace this upper limit by infinity with small error. Thus, adding the symmetric contribution from small $N - M \ll N$, one obtains

$$\dot{\psi}_d(N) = H_s\psi(N) \qquad (N \gg z) \tag{13}$$

The contribution from M values of order N gives rise to relative corrections which are shown in Appendix B to be of order $(z/N)^{1/2}$ when $N < \bar{N}$ and $(z/\bar{N})^{1/2}$ when $N > \bar{N}$.

This result, exact in the limit of very large $\bar{N}/z$, states that the instantaneous dead MWD is a copy of the living MWD for almost all chains. Its physical interpretation is very clear. Most terminations involve a short–long living pair which produces a dead chain of length equal almost exactly to that of the long living chain. But each such termination occurs with a rate constant independent of the length of the long chain involved (small wins). Thus, long living chains terminate with rate constants independent of their own length. It follows that the rate at which long chains of length N are being produced in the dead population is simply proportional to the number of chains of that length in the living population. The living is copied into the dead.

The conclusion is that the major part of the normalized instantaneous dead MWD is exponential:

$$\frac{\dot{\psi}_d(N)}{R_i/2} = \frac{1}{\bar{N}_d}e^{-N/\bar{N}_d} \qquad (N \gg z) \tag{14}$$

where the mean dead chain length $\bar{N}_d$ is identical to the mean living length, $\bar{N}$ of eq 7.

Let us now determine the short chain dead MWD. Consider, for example, the regime immediately preceding z which was considered in eq 10. Substituting the form in that equation for the living distribution ψ and introducing the crossover function f of eq 1, eq 12 then leads to

$$\dot{\psi}_d(N<z) \approx \frac{\psi^2(0)}{h^3}Nk_t(N)\int_0^1 du\, u^{-\alpha}f([1-u]/u) \times \exp\{-\epsilon(u^{1-\alpha} + (1-u)^{1-\alpha})\} \tag{15}$$

after making use of the power law behavior $k_t(N) \sim N^{-\alpha}$. Now the exact expression would include also the very shortest chain regimes, where different exponents α and crossover functions f are involved. It is easily shown that these produce small corrections to the above expression (since $\alpha > 1$, the bigger chain lengths dominate the integral). The parameter ϵ is given by

$$\epsilon \equiv (N/z)^{1-\alpha} \tag{16}$$

and is small provided N is sufficiently deeply within the regime. In that case, eq 15 implies

$$\dot{\psi}_d(N) \approx \frac{\psi^2(0)}{h^3}Nk_t(N) \qquad (N \ll z) \tag{17}$$

with corrections of order ϵ. The important point is that the integral in eq 15 exists and is analytic in ϵ. An argument similar to the above in fact applies to any of the short regimes, with the same end result. For all chains much shorter than z, the instantaneous dead MWD is given by eq 17. This is our main short chain result.

The physical meaning of this expression is very different from that underlying the long chain result which derived from short–long terminations. These latter cannot, of course, produce short chains. The generation of a short dead chain of length N necessarily requires the termination of two short living chains, of lengths $N - M$ and M. In the domain $N \ll z$ there are approximately $\psi^2(0)$ such living pairs for each M (see eq 9). There are N possible M values, i.e., a total of $N\psi^2(0)$ living pairs whose terminations produce dead chains of length N. Now, for each pair, the termination rate is weighted by a factor $k_t(N-M,M)$ whose length exponent α is less than unity. Thus, the sum over all pairs is dominated by the large scales, i.e., by M of order N, and it follows that the typical rate constant for each pair is of order $k_t(N)$. This gives a net rate of order $k_t(N)\, N\psi^2(0)$.

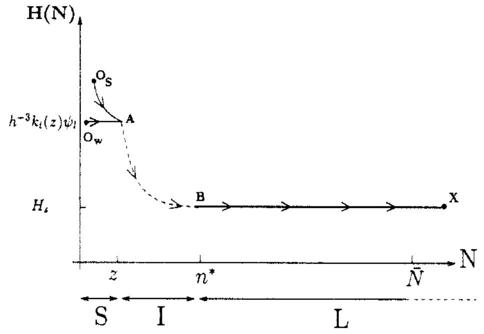

Figure 4. Autoacceleration regime. The reaction field, $H(N(t))$, experienced by a single macroradical as its length $N(t)$ increases from creation (at O_S or O_W for strong or weak systems, respectively) to termination (at a typical point X). While $N < n^*$ (short region, denoted S, and intermediate region, denoted I), H is dominated by long macroradicals: $H = h^{-3}k_t(N)\ \psi_l$. The typical short chain field is $h^{-3}k_t(z)\ \psi_l$. If the macroradical escapes S without terminating, it propagates through I with very low termination probability, entering the long domain (L) at B. Point B is reached with probability $^1/_2$. While in L, H is dominated by short chains, $H = H_s$.

Using this result and our expression for the mean length $\bar{N}_d$, one finds the normalized distribution can be approximately expressed as

$$\frac{\dot{\psi}_d(N)}{R_i/2} \approx \frac{1}{\bar{N}_d}\frac{N}{z}\frac{k_t(N)}{k_t(z)} \tag{18}$$

where we have used eq 3. Thus, in all cases power law forms apply, $\dot{\psi}_d \sim N^{1-\alpha}$, with the prefactors governed by the specifics of k_t during each regime exhibited in Appendix A. For strong systems, eq 18 leads to

$$\frac{\dot{\psi}_d}{R_i/2} \approx \begin{cases} (1/\bar{N}_f^{\,2})N^{17/20} & (N < s) \\ (1/\bar{N})N/(N_{un}^{**}z)^{1/2} & (z < N < N_{un}^{**}) \\ (1/\bar{N}_d)(N/z)^{1/2} & (N_{un}^{**} < N < z) \end{cases} \tag{19}$$

where $\bar{N}_f \equiv \upsilon_p/(R_iQ_t)^{1/2}$ is the Flory length[4] discussed in part 1, and N_{un}^{**} and s are defined in Appendix A. We have taken a value for the correlation hole exponent $g \approx {}^1/_4$. In the weak case one finds

$$\frac{\dot{\psi}_d}{R_i/2} \approx \begin{cases} (1/\bar{N}_f^{\,2})N^{17/20} & (N < s) \\ (1/\bar{N}_d)(N/z) & (s < N < z) \end{cases} \tag{20}$$

IV. Discussion

We conclude with a general discussion of the living and instantaneous dead MWDs which have been calculated in this paper, comparing their forms to those predicted by the classical Flory theory.

Living MWD. The living MWD ψ depends on the reaction field H whose structure was analyzed in detail in part 1; in steady state $\psi(N) \propto \exp\{-\int_0^N H\}$. A helpful point of view is that of a macroradical as it grows from initiation to termination at constant velocity υ_p. In Figure 4 the history of the reaction field experienced by such a radical is shown schematically. The field acting upon it is equal to its termination probability per unit time. While its length is less than n^*, the dominant contribution to this field is due to long chains which number ψ_l and are in the overwhelming majority: $H(N) = h^{-3}k_t(N)\,\psi_l$ when the macroradical has length N. During the short domain, H is extremely large; shortly after this domain comes to an end (just beyond the point A in Figure 4, when N has a value several times z), the total termination probability has already reached a value of almost $^1/_2$. Then, during the "intermediate" region (AB) the field drops drastically; $H \sim N^{-3/2}$ due to the increasing constraint of entanglements as the radical grows. Termination is most unlikely, while in AB and by its end (point B, when $N = n^*$) the total termination probability has reached $^1/_2$. That is, $\psi(n^*) = \psi(0)/2$. At this point, the ever-decreasing reaction field due to the long chains drops below that due to the short, $H = H_s = h^{-3}\int_0^\infty k_t\psi$, and the field remains at this constant value H_s thereafter. Exactly 50% of initiated macroradicals survive to enter the long domain which begins at B. These now experience a constant termination probability per unit time and terminate at a typical point X. The total termination probability while long is exactly $^1/_2$. The equality of total termination probabilities in the short and long domains reflects the fact that all terminations involve one short and one long macroradical.

Thus, by the time a growing radical reaches the length n^*, its own mobility is so reduced by entanglements that its reaction rate with the immobile long living chains becomes less than that with the small number of very mobile short living chains. Notice that were it not for these short chains the field would continue to drop to much lower values of typical magnitude $H \approx h^{-3}k_t(\bar{N})\,\psi_l$ which would induce a much stronger autoacceleration.

The above behavior of the field H leads to the expressions for the living MWD ψ of eqs 7 and 8. At any instant, most living chains are long and are experiencing the constant field H_s. Thus, in some sense one recovers Flory's famous equal reactivity hypothesis, leading to an exponential distribution for almost all of the living population. Meanwhile, the much higher field experienced by short chains is such that ψ drops by a factor of order unity over a very short width z. This very steep drop is required in order to sustain the short–long termination rate as the dominant contribution. The expression of eq 8 reveals a crucial property of the short distribution: its shape is *independent* of the initiation rate R_i; i.e., R_i only appears in the prefactor $\psi(0) = R_i/\upsilon_p$.

Instantaneous Dead MWD. The principal conclusion of this paper is that the living MWD is *copied* into the dead for long chains. The physical reasons were discussed after eq 13 which describes the situation succinctly: the constant reaction field means long chains of a given length terminate at a rate proportional to their number in the living population. Thus, most of the instantaneous dead MWD is a Flory distribution whose mean length is exactly that calculated in part 1 for the living MWD:

$$\frac{\dot{\psi}_d(N \gg z)}{R_i/2} = \frac{1}{\bar{N}_d}e^{-N/\bar{N}_d}, \quad \bar{N}_d = \frac{\upsilon_p{}^2h^3 2\ln 2}{R_i\int_0^\infty k_t} \approx \frac{1}{R_i\tau_{auto}}\phi^y(1-\phi)^2 \qquad (21)$$

where[1] the exponent $y \approx 1$, $\tau_{auto} = g(\epsilon, N_e{}^m)Q_t/Q_p{}^2$ is the width of the autoaccelerating regime, $\upsilon_p = Q_p(1-\phi)$, and g is a function whose form is different for the weak and strong cases. For a typical system, PMMA at about 100 °C, one has $\bar{N}_d \approx 10^4$ as discussed in part 1. The conversion dependence of $\bar{N}_d$ as predicted by the above expression is shown in Figure 5; $\bar{N}_d$ is strongly peaked at $\phi = \phi_{inf} = y/(2 + y)$ which coincides with the inflexion point in $\phi(t)$ (discussed in part 1) since $\dot{\phi} = R_i\bar{N}/2$. The experimental dependence shown in Figure 2 is qualitatively similar, though one does not anticipate close agreement as the polymerization approaches completion since our theory in this region is relevant only to $T > T_g$ experiments where T_g is the melt glass transition temperature (see part 1). The observed and predicted values of ϕ_{inf} are considerably different (about 0.55 and 0.35, respectively). This may be due to transients during the approach to full autoacceleration, or it may reflect the unreliability at high conversions of the semidilute power laws used to evaluate y. This point was discussed in part 1; the first expression for $\bar{N}_d$ in eq 21 is claimed to be exact at high enough conversions, but not the second.

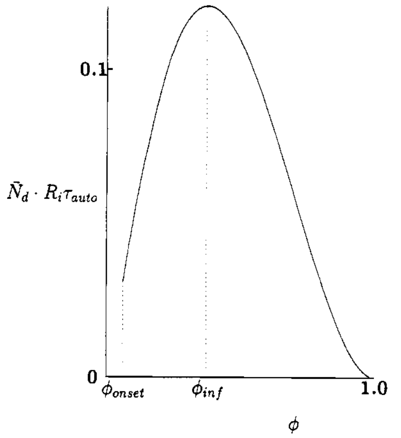

Figure 5. Predicted instantaneous mean dead chain length (scaled by $(R_i\tau_{auto})^{-1}$) as a function of conversion ϕ (strong system). The maximum of $\bar{N}_d$, at $\phi \approx 0.36$, coincides with the inflexion point of the conversion profile $\phi(t)$. ϕ_{onset}, discussed in ref 1, is the conversion at autoacceleration onset.

This exponential distribution is very different from that predicted by the Flory theory. Quite apart from the completely different expressions for mean chain length, in the classical theory the dead distribution $\dot{\psi}_d \propto N\exp\{-N/\bar{N}_d\}$ collects an extra combinatorial prefactor N relative to the exponential living distribution. This is because there are N ways to choose living pairs $N - M$ and M so as to generate a dead chain of length N. There is no such prefactor here, due to short–long domination: during autoacceleration the only way to generate a long dead chain of length N is via the termination of a long living chain of about the same length with a second very short chain. There is essentially only one way to do this (i.e., the number of ways does not depend on N).

These differences are reflected by the fact that the mean dead chain length is twice the living ("kinetic") length in Flory theory, while here they are identical. Further, since we predict (as far as the long chains are concerned) a monotonic decreasing distribution, while in the classical theory $\dot{\psi}_d$ is peaked at $\bar{N}_d$, our distribution is broader. It is characterized by a polydispersity index[13] $\bar{M}_w/\bar{M}_n = 2$ as compared to a value of $^3/_2$ in the Flory theory.

Finally, the instantaneous dead MWD for short chains exhibits power law behavior as given in eqs 19 and 20. That is, scrutinizing the MWD down to scales as small as z, one finds the exponential long chain form crosses over to algebraic behavior, decaying to zero at the origin. The powers involved reflect the very different termination kinetics which prevail for short chains where the length exponent α in $k_t \sim N^{-\alpha}$ is always less than unity. This means that sums over many pairs of different lengths are

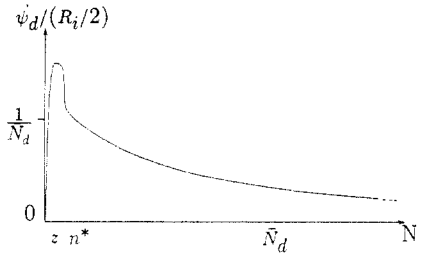

Figure 6. Schematic of theoretical normalized instantaneous dead distribution. Chains longer than z are distributed identically to the living distribution (exponential or Flory distribution). The shortest chains are power law distributed. Between the short and long distributions, a peak is exhibited around $N = z$. For a typical PMMA polymerization at $\phi = 0.5$, for example, the scales characterizing the distribution have the following numerical values (number of chain units): $z \approx 100$, $n^* \approx 1500$, and $\bar{N}_d \approx 5000$.

dominated by the large length scales (there is no short–long domination). Thus the rate at which dead chains of length N are being produced involves the same combinatorial factor N as in the classical theory, but this time with the appropriate weighing $k_t(N)$. The net power is $N^{1-\alpha}$.

Now for chains shorter than but of order z the instantaneous dead MWD increases as a power, while it decreases for lengths greater than but of order z (see eqs 11 and 13). The conclusion is that $\dot{\psi}_d$ must undergo a fractional change of order unity over a scale of order z: a peak exists around $N = z$ whose width is of order z. From experimental values for PMMA, one estimates a value $z \approx 100$ at the height of autoacceleration for conditions well removed from the glass transition, though this value may be significantly reduced when glassy effects influence even the short scales (see part 1). This and the other features discussed above are reproduced in the schematic representation of the normalized instantaneous dead MWD shown in Figure 6.

The above conclusions are somewhat modified when "disproportionation" processes are important.[4] Such events, which tend to be more frequent at higher temperatures, are terminations in which the two reacting living chains generate two chains in the dead population of the same length; the reacting living chains fail to join together as they would do in a "normal" termination. Assuming the probability of disproportionation (given that a termination event has occurred) is independent of chain length, to obtain the instantaneous dead population in the case where all terminations are disproportionation events, one may start from the distribution *without* disproportionation (Figure 6) and then simply decompose each dead chain into the short and long pair which combined to produce it. Clearly, therefore, the long chain part of the distribution is unaffected, while the short chain part will now be given not by eq 17 but rather by $\dot{\psi}_d(N) \approx k_t(N)\ \psi(N)\ \psi_l/h^3$. This is just the rate at which short living chains of length N terminate with long ones and is now the dominant contribution to the dead short chain population. Since $\psi(N)$ changes by a factor of order unity in the short domain, it follows that $\dot{\psi}_d \sim k_t(N)$. Thus, the short distribution diverges at the origin and its shape is that of $k_t(N)$ (see Figure 5 of the preceding paper in this issue[1]). The rate of production of short chains is now equal to that of long chains, $R_i/2$. Generally, given that the disproportionation probability is p, the net instantaneous distribution is simply a combination of that with and that without disproportionation in the ratio of p to $1 - p$. These issues will be dealt with more exhaustively in a future study.

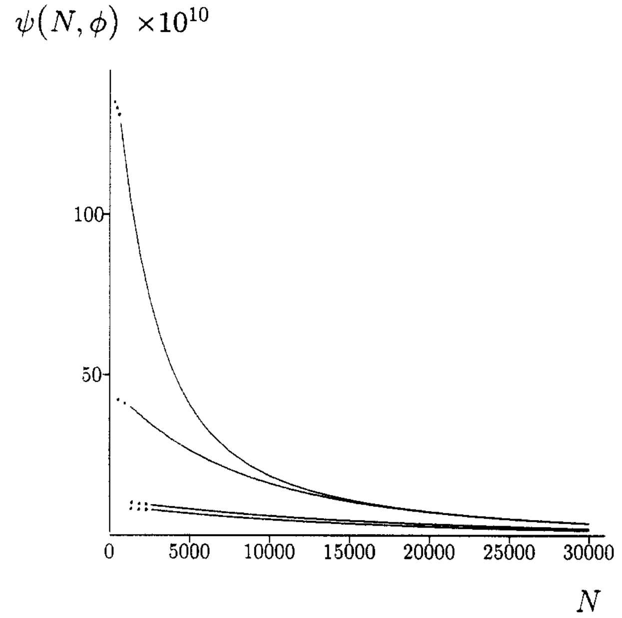

Figure 7. Theoretical cumulative MWDs at conversions ϕ = 0.38 (lowest curve), 0.48, 0.83, and 0.9 (top curve). The MWDs were calculated using the PMMA parameter values specified in ref 1, which were estimated to correspond to the experiments of Balke and Hamielec in ref 6. Only the long chain portions ($N \gtrsim z$) of the distributions are shown.

In Figure 7, cumulative MWDs $\psi_d^{\text{cum}}(N)$ are plotted for the long chain part of the distribution at several conversions. The short chain part has been omitted, being determined not just by those short chains produced during autoacceleration regimes but also by those produced during preautoacceleration regimes. For long chains the instantaneous MWd is exponential whence $\psi_d^{\text{cum}} = \int_{\phi_0}^{\phi} d\phi'\ \dot{\psi}_d/\dot{\phi} = \int_{\phi_0}^{\phi} d\phi'\ e^{-N/\bar{N}}/\bar{N}^2$. We have used[1] $\dot{\phi} = (R_i/2)\bar{N}$. The plots of Figure 7 were obtained after using the result for $\bar{N}$ as a function of ϕ in ref 1 (eq 37, for a strong system) and numerical integration, with $\phi_0 = \phi_{\text{onset}}$ (the conversion at autoacceleration onset). The parameters were estimated to correspond to the PMMA experiments of Balke and Hamielec[6] for which cumulative MWDs are shown in Figure 1. However, direct comparison with the "long chain" part of their MWDs is very difficult since as discussed previously the relation of the parameter υ to chain length is unknown.

This paper has emphasized the instantaneous MWD. In contrast to the cumulative distribution, which is a complex convolution of many distributions of this type, the instantaneous MWD is predicted in many respects to be a universal object. It is our hope that the present work will motivate further experimental effort to establish its precise forms during autoacceleration.

Appendix A. Short Chain ($N < z$) Reaction Kinetics

In "strongly reacting" systems,[10] z is identified with the entanglement threshold[14,15] $N_e(\phi)$: $z = N_e^m\phi^{-\gamma}$ where N_e^m is the melts value and experimental values of γ lie in the range[15–17] $1 \lesssim \gamma \lesssim 1.3$. There are three "short" regimes:[10,18]

$$k_t(N) \approx \begin{cases} Q_t h^3 N^{-3g/5} & (N < s) \\ Q_t h^3 s^{-3g/5} & (s < N < N_{\text{un}}^{**}) \qquad \text{(strong)} \\ k_t(z)\ (z/N)^{1/2} & N_{\text{un}}^{**} < N < z \equiv N_e \end{cases} \tag{A1}$$

where Q_t is the local rate constant of the reactive group and s is the number of monomers per semidilute blob of size[14,19] ξ. The "correlation hole" exponent[20–22] $g \approx 0.27$. The characteristic scale $N_{\mathrm{un}}^{**} \approx \epsilon^{-2}\phi^{-(5+6g)/4}$, where $\epsilon \equiv Q_t t_h$ (t_h is the monomer relaxation time), defines the onset of diffusion-controlled (DC) but *unentangled* kinetics.[10] For "weakly reacting" polymer solutions the route is somewhat different, with $z = N_{\mathrm{ent}}^{**} \approx (N_e{}^{m}/\epsilon)^{2/3}\phi^{-(8\gamma+6g+5)/12}$ and there being only two short regimes:

$$k_t(N) \approx \begin{cases} Q_t h^3 N^{-3g/5} & (N < s) \\ Q_t h^3 s^{-3g/5} & (s < N < z \equiv N_{\mathrm{ent}}^{**}) \end{cases} \quad \text{(weak)} \qquad \text{(A2)}$$

Appendix B. Long Chain ($N \gg z$) Dead MWD: Corrections

In this appendix corrections are evaluated to the result of eq 13, $\dot{\psi}_d = H_s\psi$, which states that the long chain instantaneous dead MWD copies the living MWD. We will make use of the estimate $h^3 H_s \approx z k_t(z)\, \psi(z)$ (see eq 5).

Using the $M \leftrightarrow N - M$ symmetry of the integral in the basic expression for $\dot{\psi}_d$ (eq 12), one has

$$\dot{\psi}_d(N) = \frac{1}{h^3}\int_0^\infty \mathrm{d}M\, k_t(M)\, \psi(N-M)\, \psi(M) - \frac{1}{h^3}\int_{N/2}^\infty \mathrm{d}M\, k_t(M)\, \psi(N-M)\, \psi(M) + \frac{1}{h^3}\int_0^{N/2} \mathrm{d}M\, [k_t(N-M,M) - k_t(M)]\, \psi(N-M)\, \psi(M) \qquad \text{(B1)}$$

The first integral gives the overall leading contribution, $H_s\psi(N)$, after approximating $\psi(N-M)$ by $\psi(N)$, plus a correction term. This correction is an integral dominated by $M \approx \bar{N}$, producing a relative correction to $H_s\psi(N)$ of order $(z/\bar{N})^{1/2}$. The second integral in eq B1 is dominated by its lower cutoff and gives a relative correction of order $(z/N)^{1/2}$.

The third integral is a little more complex. Its magnitude is governed by the properties of the crossover function f of eq 1, $f \equiv k_t(N,M,\phi)/k_t(N)$. It is shown in ref 5 that $k_t(N,M,\phi)$ has the following structure:

$$k_t(N>z,M,\phi) \approx \begin{cases} k_t(M)\, f(N/z) & (M < z) \\ k_t(M)\, f(N/M) & (M > z) \end{cases} \qquad \text{(B2)}$$

This is a generalization of the expression given in eq 1 which dealt with the simplest case when N and M belong to the same reaction kinetics regime. Thus, the third integral appearing in eq B1 is expressed approximately as

$$\frac{1}{h^3}\int_0^z \mathrm{d}M\, k_t(M)\, [f((N-M)/z) - 1]\psi(N-M)\, \psi(M) + \frac{1}{h^3}\int_z^{N/2} \mathrm{d}M\, k_t(M)\, [f((N-M)/M) - 1]\psi(N-M)\, \psi(M) \qquad \text{(B3)}$$

The important feature[5] of the function f is that it approaches unity for large arguments, according to a regime-dependent crossover exponent η: $f(u \gg 1) \approx 1 + u^{-\eta}$. For all reaction regimes, the exponent exceeds $^1/_2$. One then finds that both integrals in eq B3 are dominated by their upper limits and give relative corrections of order $(z/N)^\eta$ and $(z/N)^{1/2}$, respectively, to the leading order result. In summary

$$\dot{\psi}_d(N \gg z) = \begin{cases} H_s\psi(N)\, \{1 + O(z/N)^{1/2}\} & (N < \bar{N}) \\ H_s\psi(N)\, \{1 + O(z/\bar{N})^{1/2}\} & (N > \bar{N}) \end{cases} \qquad \text{(B4)}$$

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