5240 *Macromolecules* **1998,** *31,* 5240−5254

Non-Steady State Free Radical Polymerization Kinetics at High Conversions: Entangled Regimes

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Received November 3, 1997; Revised Manuscript Received March 24, 1998

ABSTRACT: We present a theory of non-steady state free radical polymerization kinetics at high conversions where entanglements are present. Our immediate aim is to explain apparently infinite experimental living chain lifetimes at conversions that are high, but very far from the onset of glassy behavior. In these "posteffect" studies, the time dependence of the total number of living chains is measured, after the steady state is interrupted by switching off primary radical production at $t = 0$. We find that infinite lifetimes are inevitable in posteffect when entanglements are present. Our starting point is a previous theoretical study of steady state entangled polymerizations according to which the principle termination mechanism for the majority long entangled chains is provided by the small population of short mobile unentangled chains. In posteffect, we find that the entire short living chain population disappears after a time scale $\tau_{\text{short}} \approx z/v_p$, where z is the conversion-dependent threshold for entanglement-dominated reaction kinetics and v_p is the rate at which monomers add to a living chain. For $t < \tau_{\text{short}}$ the situation is essentially unchanged from steady state and the terminated fraction R_t grows linearly in time t. But by τ_{short} all short chains have either grown to become long or have terminated through interpolymeric radical−radical reactions. Consequently, the net termination rate is drastically suppressed for $t > \tau_{\text{short}}$, decaying as $1/t^{1/2}$. Correspondingly, $R(t)$ increases as $t^{1/2}$. At the longest times, $t > \tau_{\text{rad}}$, where τ_{rad} is the mean steady state living chain lifetime, termination saturates: in the presence of entanglements, the living population is infinitely long-lived and the final terminated fraction is of order $(z/\bar{N})^{1/2} \ll 1$, where $\bar{N}$ is the steady state living chain length. Our intermediate time prediction, $R(t) \sim t^{1/2}$, is consistent with experiment.

I. Introduction

Bulk free radical polymerizations (FRPs) exhibit complex behavior[1−3] at high values of the conversion (the fraction of initially present monomer that has been polymerized). Above a certain system-dependent conversion, steady state polymerization rates[4,5] start to increase and subsequently (typically at conversions in the range 20−40%) may reach levels 1 order of magnitude greater than their initial values at zero conversion. The regime of rapid increase in polymerization rates, molecular weights, and heat production is generally labeled by the somewhat nebulous term[1−10] "gel effect". Polymerization rates are said to autoaccelerate.

This paper is concerned with *non-steady state* behavior at these high conversions. Our immediate aim is to explain the remarkable findings of a number of "posteffect" studies[11−13] that exhibit *infinite* macroradical lifetimes at high conversions. In these experiments, the FRP is run in steady state for minutes or hours until a certain conversion ϕ is attained. At $t = 0$, the radical production rate R_i is then set to zero by suddenly switching off the ultraviolet source. The total number of macroradicals, $\psi_l(t)$, is thereafter monitored by electron spin resonance (ESR), as shown in Figure 1 for one set of experiments. Now at lower conversions, $\phi \lesssim 20\%$, $\psi_l(t)$ decays to zero after a time scale of the order of seconds. This is as expected. What is remarkable is the behavior at higher conversions: the living chain population is apparently *infinitely* long-lived. It is essential to stress that infinite lifetimes in the PMMA (poly(methyl methacrylate)) systems of Figure 1, for example, occur at conversions as low as $\phi \approx 20\%$. At these experimental temperatures, a 20% solution of PMMA plus MMA solvent is a perfectly ordinary thermodynamically stable solution of moderate viscosity. Its properties are not remotely close to those of a solution approaching glassiness. For some reason the macroradical population cannot decay, or at least exhibits extraordinarily long lifetimes, even when its environment is nonglassy.

In this paper we develop a theory of these posteffect dynamics. The authors of ref 11 attributed the above phenomena to microheterogeneities: small glassy regions in the FRP mixture where macroradical mobility essentially vanishes. We find there is no need to invoke such effects: infinite lifetimes emerge naturally from a straightforward theoretical treatment applying basic principles of polymer physics. We show that infinite lifetimes arise in posteffect if macroradicals, or "living chains", are *entangled*[14−16] in their dead chain surroundings. Our starting point is a previous theoretical examination of *steady state* properties of entangled bulk FRPs by the present authors.[17] A number of other works have also investigated the role of entanglements in steady state FRP, both theoretically[18−22] and experimentally.[10]

We will consider bulk FRPs (initial reaction mixture pure unsaturated monomer plus trace initiator), and chain-transfer effects[1] will be neglected. The latter is

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S0024-9297(97)01616-1 CCC: $15.00

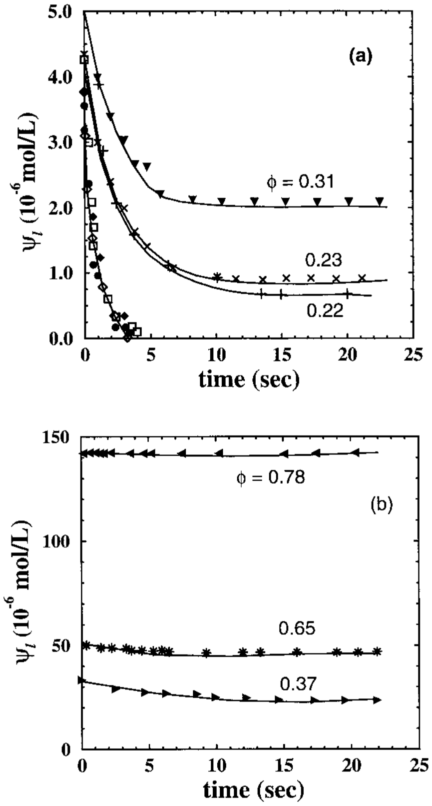

Figure 1. ESR measurements by Zhu et al., Figure 3 of ref 11. Bulk MMA (i.e., no solvent) at 25 °C, with 5% weight AIBN, initiated by ultraviolet radiation. Living chain density $\psi_l(t)$ shown versus time t after switching off radical production at $t = 0$ after the FRP had been run in steady state up to some conversion ϕ ("posteffect" decay). Each curve corresponds to a different ϕ: (a) $\phi = 0$ (filled circle), $\phi = 0.05$ (open diamond), $\phi = 0.100$ (filled diamond), $\phi = 0.13$ (empty square), $\phi = 0.22$, 0.23, 0.31 as indicated; (b) $\phi = 0.37$, 0.65, 0.78 as indicated. For conversions 0.22 and above, the living population does not decay to zero; only a short-lived subpopulation decays. By $\phi = 0.65$, this subpopulation is a very small fraction of the total living population.

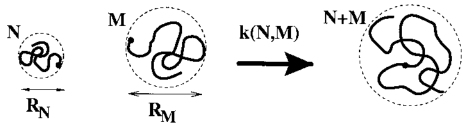

Figure 2. Each termination event entails the interpolymeric reaction of two living chains of lengths N and M according to second order rate kinetics with rate constant $k(N,M)$. The radical ends combine to produce a dead chain of length $N + M$. When the reacting chains are strongly entangled, theory predicts $k(N,N) \approx DR_N$, where R_N is the coil size and D is the polymer center-of-gravity diffusivity. This leads to $k(N,N) \sim 1/N^{3/2}$.

a good approximation[1] for PMMA, and accordingly all experimental data we consider here (e.g., those in Figure 1) concern PMMA systems. We consider conversions high enough that entanglements are present but exclude the highest values where glassy effects begin (e.g., ϕ approaching 0.78 in Figure 1). Thus, for example, "residual termination" processes[23,24] (chain termination through chain growth) are irrelevant. These are only important when center of gravity chain diffusivity is massively suppressed as in near-to-glassy environments. A future study will address glassy FRPs.

Let us consider the experiment of Figure 1 more carefully by first briefly reviewing the basic processes underlying FRP.[1] Primary radicals (which in our continuous framework are living chains of length "zero", $N = 0$) are generated at rate R_i per unit volume. Each such newly born living chain then proceeds to grow, its highly reactive radical end attacking unsaturated monomer in its environment, until being removed from the living population by reaction with another living chain, as depicted in Figure 2. In this "termination" reaction the two radical end groups recombine, resulting in one dead chain.[25] Dead chains are the final polymer product and vastly outnumber living chains. The tiny living chain population is constantly adding new dead chains to a huge reservoir of dead chain plus monomer solvent, which is the environment in which the living chain kinetics are occurring.[26] Now in steady state the total termination rate due to all interchain reactions equals R_i. But when R_i is set to zero as in posteffect, living chains are thereafter no longer being created and yet are still terminating with one another. A natural expectation[1] therefore, is that $\psi_l(t)$ should decay to zero after a time of the order of $\tau_{\rm rad}$, the steady state mean living chain lifetime,

$$\tau_{\rm rad} = \bar{N}/v_{\rm p}, \qquad v_{\rm p} \equiv (k_{\rm p}/A_0)(1 - \phi)a^{-3} \qquad (1)$$

Here $\bar{N}$ is the mean living chain length under conditions of steady state (which pertained until $t = 0$) and $v_{\rm p}$ is the "propagation velocity", namely, the number of monomers adding to a growing living chain per second. ($v_{\rm p}$ is expressed in terms of the conventionally defined propagation rate constant $k_{\rm p}$ and the volume fraction of unpolymerized monomer, $1 - \phi$, with a^3 being the monomer volume and A_0 Avogadro's number.) At lower conversions, this expectation is borne out by experiment: the decay times in Figure 1 are of order 1 s, which if equated to $\tau_{\rm rad}$ would correspond to reasonable values[1] of $\bar{N} \lesssim 1000$ (typically,[1] $v_{\rm p} \approx 10^3$ s^{-1}). But at higher conversions, after an initial transient during which a certain fraction of the living population disappears, termination apparently ceases: the remaining chains are extremely long-lived. As conversion increases, the long-lived chains constitute an increasingly large fraction of the total living population. At the highest conversions, virtually the entire living population is unable to decay.

Qualitatively, we will see that the above behavior occurs because in posteffect the mean living chain length is increasing with time, since all unterminated chains are growing with velocity $v_{\rm p}$ and yet new chains of length $N = 0$ are no longer being generated as in steady state. Consequently, the net termination rate is decreasing in time. It happens that in the presence of entanglements, which strongly suppress living chain mobility,[14−16] this decrease is so rapid that the living population cannot decay. To quantify this, consider how the bimolecular termination rate constant, $k(N,M)$, depends on the lengths N and M of a pair of reacting living chains (see Figure 2) at conversions above a threshold value ϕ_e at which entanglements onset. Note that conversion ϕ and the polymer concentration in the solution of dead polymer plus unreacted monomer are one and the same. (Throughout this study we employ units where the volume of one monomer, a^3, equals unity; thus dead chain concentration, $c = \phi/a^3$, is equal to dead chain volume fraction ϕ.) Now for a solution of chains of length $N_{\rm dead}$, this entanglement threshold approximately obeys[16,27−30] the empirical relation $\phi_e \approx N_e^m/N_{\rm dead}$ where N_e^m is the entanglement chain length threshold in the melt. But in FRP we have a broad distribution of living chain lengths N; if the conversion is ϕ, we thus expect k to be very different for "long" entangled living chains, $N > N_e(\phi)$, as compared to "short" unentangled ones, $N < N_e(\phi)$. Here $N_e(\phi) \approx N_e^m/\phi$ is the chain length entanglement threshold at ϕ.

Consider first the case $M = N$. According to theory,[31] for entangled chains with highly reactive end groups such as radicals k exhibits a diffusion-controlled form, $k \approx DR$, where D is the center of gravity diffusivity and R is the root mean square (rms) coil size (see refs 32−34 for detailed discussions). In the reptation theory of entangled dynamics[14,15] we have $D \sim 1/N^2$ and $R \sim N^{1/2}$. Thus,[31,32] $k \sim 1/N^{3/2}$. This is the first of three predicted general properties

$$(1)\quad k(N,N) \sim \frac{1}{N^{3/2}} \qquad (N > z)$$

$$(2)\quad k(N,N) \sim \frac{1}{N^{\theta}}, \qquad \theta < 1 \qquad (N < z)$$

$$(3)\quad k(N,\infty) \equiv k(N) = Ak(N,N) \tag{2}$$

where A is a constant of order unity and z is the threshold living chain length for entanglement-dominated diffusion controlled (DC) kinetics. In the simplest case, $z = N_e(\phi)$. (We employ the distinct symbol z because there exists a second possible case[31] where z is somewhat greater than $N_e(\phi)$.) As we will see below, the crucial point is that k decays more rapidly than $1/N$ for long entangled chains $N > z$. This contrasts with short chain kinetics,[31,35] $N < z$, where k decays *less* rapidly than $1/N$. (In fact, there are a number of $N < z$ regimes with different exponents θ, all of which are less than unity. For simplicity in what follows we assume one short chain exponent; this does not alter any major conclusions.) Property 3 states that[36,37] the rate constant $k(N)$ between two chains, one of which is much longer ($M = \infty$) than the other, is dominated by the short more mobile chain (N) and is essentially equal to the rate constant between two short chains. For long chains, we can thus write

$$k(N) = k(z)\left(\frac{z}{N}\right)^{3/2} \qquad (N > z) \tag{3}$$

where $k(z)$ emerges as a characteristic short chain termination rate constant. These results for $k(N,M)$ are theoretical predictions. For general discussions of the experimental situation, the reader is referred to refs 31 and 38. We note that no quantitative data on molecular weight dependencies of k are available (to our knowledge) at higher concentrations, in particular at concentrations where entanglements are important and $k \sim 1/N^{3/2}$ is predicted. We will see below that FRP posteffect data in fact constitute a test of this law, albeit a somewhat indirect one.

One can now begin to understand the origin of the infinite lifetimes quantitatively. At $t = 0$, just after irradiation has been switched off, the living chains follow a certain steady state molecular weight distribution (MWD) $\psi^0(N)$ of width $\bar{N}$. Thereafter, living chains grow with velocity v_p, but new chains are no longer being created; thus, after a time $t \gg \tau_{rad}$ the entire MWD has shifted an amount v_pt in the $+N$ direction (see Figure 4e), which is much greater than its width $\bar{N}$. That is, the mean chain length is approximately v_pt and is much greater than the spread in chain lengths, $\bar{N}$: the MWD is being driven to an increasingly *monodisperse* distribution and $k(N,M)$ is approximately the same for every pair N, M. The termination kinetics are thus

$$\frac{d\psi_l}{dt} \approx -k(v_pt,v_pt)\psi_l^{\,2}, \qquad k(v_pt,v_pt) \sim \frac{1}{t^{3/2}} \qquad (t \gg \tau_{rad}) \tag{4}$$

These are the simple kinetics of Flory's theory of FRP,[1] which neglects chain-length dependence of k. There is one new feature, however: k is now *time-dependent*, being evaluated at the current mean chain length v_pt. If the FRP mixture is in the entangled regime, the scaling behavior of eq 3 implies $k \sim 1/t^{3/2}$ decays more rapidly than $1/t$. Because of this fast decay, it is simple to show that under the kinetics of eq 4 ψ_l *never* decays to zero. The solution at $t = \infty$ can be written (t_0 is some reference time)

$$\frac{1}{\psi_l(\infty)} - \frac{1}{\psi_l(t_0)} = \int_{t_0}^{\infty} dt\, k(v_pt,v_pt) \tag{5}$$

Since $k \sim 1/t^{3/2}$, the integral converges to a finite positive constant and thus the asymptotic number of living chains $\psi_l(\infty)$ is a finite fraction of the original number $\psi_l(0)$. It is now clear why the $N > z$ kinetics of eq 2 are so fundamentally different from the kinetics for $N < z$, for which $k \sim 1/N^{\theta}$. In that case the time dependence in eq 5 would be $k \sim 1/t^{\theta}$ with $\theta < 1$; the integral now diverges, $\psi_l(\infty)$ thus vanishes, and the living population decays completely. This is the low conversion behavior we see in Figure 1. For this reason, the onset of infinite posteffect lifetimes corresponds to the onset of entanglement-dominated living kinetics. This is consistent with the data of Figure 1, where such effects begin at $\phi \approx 20\%$. The theory we develop below will identify the decay time during the initial transient as τ_{rad} (for nonglassy conditions); accepting this, a value $\bar{N} \approx 3000$ is implied at $\phi \approx 20\%$. Taking $N_e^m \approx 300$ for PMMA,[16] this implies $\phi_e \approx 10\%$. At $\phi = 20\%$, one has $\bar{N}/N_e \approx 2$, which is a reasonable value for the onset of entanglement-dominated termination kinetics given that the dead chains include a significant fraction produced by earlier living chain regimes with lengths much less than $\bar{N}$.

We remark that the "infinite" lifetimes emerging from the following analysis in reality indicate that some very slow and normally irrelevant process will determine the actual lifetime. For example, in the context of our predicted infinitely slow net termination rates, even very weak chain transfer effects (neglected here) may ultimately determine the actual lifetime.

In the following, a central role will be played by the living chain MWD, to which ψ_l is related as follows:

$$\psi_l(t) = \int_0^{\infty} dN\, \psi(N,t) \tag{6}$$

Here $\psi(N,t)$ is the number of living chains at time t whose degree of polymerization or "length" equals N (per unit volume per unit chain length interval). $\psi^0(N)$ is the same in the steady state.

Before detailed calculation, let us establish a few mathematical preliminaries to be used frequently in the calculations that follow. Any integral of the large N form, $k \sim 1/N^{3/2}$, is dominated by smaller values of N

and would of course diverge if continued down to $N = 0$. There is a natural cutoff at $N \approx z$ where the integrable form $k \sim N^{-\theta}$ takes over. Any integral of this short chain form is now dominated by *large N* values. It follows that if one integrates *through* z, the scale z itself dominates. Typical integrals of this type which will arise are

$$\int_0^\infty \mathrm{d}N\ k(N) \approx zk(z), \qquad \int_{v_\mathrm{p}t}^\infty \mathrm{d}N\ k(N)\ \psi(N,t) \approx zk(z)\ \psi(z,t) \qquad (v_\mathrm{p}t \ll z) \quad (7)$$

These are order of magnitude estimates, valid to within numerical prefactors of order unity. The second integral is dominated by the function k, which decays sharply for large values $N \gg z$, since for such N values $\psi(N,t)$ is broad and slowly decaying with width $\bar{N} \gg z$ (see below). On the other hand, when the lower limit is much greater than z but much less than $\bar{N}$, the same integral is dominated by this lower limit,

$$\int_{v_\mathrm{p}t}^\infty \mathrm{d}N\ k(N)\ \psi(N,t) \approx \psi(v_\mathrm{p}t,t) \int_{v_\mathrm{p}t}^\infty k \qquad (z \ll v_\mathrm{p}t \ll \bar{N}) \quad (8)$$

The integrable algebraic decay $k(N) \sim 1/N^{3/2}$ has an effective width equal to the lower limit $v_\mathrm{p}t$. In other words, $\int_{v_\mathrm{p}t}^{N_\mathrm{upper}} k$ converges to $\int_{v_\mathrm{p}t}^\infty k$ for values of N_upper of order or greater than $v_\mathrm{p}t$. Hence, when k is integrated against ψ of width $\bar{N}$ much greater than $v_\mathrm{p}t$, the value of the function ψ at the lower limit $v_\mathrm{p}t$ is picked out. This is demonstrated systematically, for a specific form of ψ, in Appendix C (eq C5). Finally, we will frequently employ the following approximate equalities:

$$\psi(N_1,t) \approx \psi(N_2,t) \qquad (|N_1 - N_2| \ll \bar{N}), \qquad \psi_1 \approx \psi(0,t)\bar{N} \quad (9)$$

Here ψ_1 is estimated as the width of ψ, namely $\bar{N}$, times the typical "height" $\psi(0,t)$.

In section II we review high conversion FRP in steady state. When entanglements dominate, long entangled living chains are so immobilized that their fastest termination mechanism is with the far more mobile short unentangled chains, despite the fact that very few short chains exist. The domination of "short−long" terminations is crucial to the events during posteffect. In sections III and IV posteffect is studied in detail for entangled systems. The argument leading to eq 5 is refined considerably. For example, in deriving eq 5, we simply assumed that the MWD reaches the $t \gg \tau_\mathrm{rad}$ situation of Figure 4e in the first place without having suffered significant termination in the early stages, $t < \tau_\mathrm{rad}$; this is a more subtle point, addressed in section III. We show that, in fact, negligible termination occurs during this period because, after a brief transient, the short chains no longer exist, having all either terminated or grown to become long. In section V our results are discussed and compared with experiment.

II. Steady State at High Conversions: Entangled Regimes

In this section we briefly review steady state FRP at conversions high enough that living chain termination kinetics are dominated by entanglements (see ref 17 for detailed accounts.) That is, the mean living chain length $\bar{N}$ is well above the threshold z of eq 2. This means *almost all living chains are long*, i.e., have lengths $N > z$. Thus the number of long chains approximately equals the total number of living chains, ψ_1^0. Let ψ_s^0 be the number of chains which are short, $N < z$. This is a very small fraction of the total living population:

$$\psi_\mathrm{s}^0 \approx \frac{z}{\bar{N}}\,\psi_1^0, \qquad \frac{z}{\bar{N}} \ll 1 \quad (10)$$

To estimate the number of short chains, we have assumed (as justified below) a broad living MWD. The ratio of the numbers in each population, $z/\bar{N}$, is the parameter whose smallness defines this regime.

A principal conclusion of ref 17 was that steady state termination kinetics are dominated by reactions involving one short and one long living chain. To see why, let us estimate the ratio of the total termination rates due to, respectively, long−long and short−long reactions. Now long chains have lengths of order $\bar{N}$, while the characteristic short chain length is z. Thus

$$\frac{R_\mathrm{term}^{\mathrm{long-long}}}{R_\mathrm{term}^{\mathrm{short-long}}} \approx \frac{k(\bar{N},\bar{N})\psi_1^{0^2}}{k(z,\bar{N})\psi_\mathrm{s}^0\ \psi_1^0} \approx \frac{k(\bar{N})}{k(z)}\,\frac{\bar{N}}{z} \approx \left(\frac{z}{\bar{N}}\right)^{1/2} \ll 1 \quad (11)$$

after using $k(z,\bar{N}) \approx k(z)$ (property 3, eq 2). The ratio is very small; i.e, short−long reactions dominate. Physically, typical living chains are long and their mobility is so reduced by entanglements that the far more mobile short chains (which are too small to see the entanglements) provide the fastest termination mechanism despite their small numbers. The intuitive expectation that a typical termination reaction should involve two typical living chains, i.e., two chains with lengths of order the mean chain length, is wrong: long−long reactions are "short-circuited" by short−long events. As for posteffect (see discussion in the Introduction) the crucial factor is that k decays faster than $1/N$ for large N, eq 3. Were this decay slower than $1/N$, the above ratio would be very large. Note that the contribution from terminations between short pairs, $k(z)\psi_\mathrm{s}^{0^2}$, is smaller than $R_\mathrm{term}^{\mathrm{short-long}}$ by a factor of $z/\bar{N}$.

Let us quantify these arguments by calculating the steady state living MWD, ψ^0. We define the steady state "reaction field", $H^0(N)$, to be the total reaction probability per unit time for a living chain of length N due to all other living chains M:

$$H^0(N) \equiv \int_0^\infty \mathrm{d}M\ k(N,M)\ \psi^0(M) \quad (12)$$

Consider the integral defining H^0, and recall the fact that $k(N,M)$ is dominated by the smallest of M and N. Thus for small N, for almost all M values one may replace $k(N,M) \rightarrow k(N)$, while for large N one can replace $k(N,M) \rightarrow k(M)$. This leads to the following short and long chain forms for H^0:

$$H^0(N < n_0^*) = k(N)\psi_1^0$$

$$H^0(N > n_0^*) = H_\mathrm{s}^0 \equiv \int_0^\infty \mathrm{d}M\ k(M)\ \psi^0(M) \approx k(z)\ \psi^0(0)z \approx k(z)\psi_\mathrm{s}^0 \quad (13)$$

These expressions reflect short−long domination. The field on chains shorter than the scale n_0^* (discussed below) is dominated by long ones. This field is proportional to ψ_l^0 (approximately the number of long chains) multiplied by the rate constant $k(N)$ appropriate to a reaction between a short chain of length N and a much longer one. Meanwhile, the field on long chains, H_s^0, is independent of N and approximately equal to the number of short chains in the system, ψ_s^0, multiplied by the rate constant $k(z)$ appropriate to a reaction between a short chain of order z in length and a much longer chain. We used eq 8 to obtain these asymptotic forms. They would not follow if k did not decay more rapidly than $1/N$.

The crossover from short to long field occurs at $N = n_0^*$, where the two fields are equal, giving

$$n_0^* \approx z^{1/3}\bar{N}^{2/3} \qquad (14)$$

whence $z \ll n_0^* \ll \bar{N}$.

If it is true that every termination reaction involves one short–long pair, it must follow that the total termination rate of all short chains, $R_{\rm term}^{\rm short}$, is equal to that of all long chains, $R_{\rm term}^{\rm long}$. One can indeed show this by using the asymptotic field forms from eq 13, which give

$$R_{\rm term}^{\rm short} \equiv \int_0^{n_0^*} H^0\psi^0 = \psi_l^0 \int_0^{n_0^*} k\psi^0 \approx H_s^0\,\psi_l^0,$$
$$R_{\rm term}^{\rm long} \equiv \int_{n_0^*}^{\infty} H^0\psi^0 = \int_{n_0^*}^{\infty} H_s^0\,\psi^0 \approx H_s^0\,\psi_l^0 \quad (15)$$

We were able to replace the upper limit of $\int_0^{n_0^*} k\psi^0$ by infinity with small error since the integrand has width of order z and $n_0^* \gg z$. To obtain $R_{\rm term}^{\rm long}$ we used $\int_{n_0^*}^{\infty}\psi^0 \approx \psi_l^0$ since $n_0^* \ll \bar{N}$. Thus

$$R_{\rm term}^{\rm short} \approx R_{\rm term}^{\rm long} \approx R_{\rm i}/2 \qquad (16)$$

The last equality follows because the sum $R_{\rm term}^{\rm short} + R_{\rm term}^{\rm long}$ is the total termination rate, which in steady state equals the rate of birth of living chains, $R_{\rm i}$.

The steady state MWD ψ^0 results from a balance of propagation and termination rates, as expressed by[17] the following nonlinear and nonlocal PDE:

$$v_{\rm p}\frac{\partial\psi^0}{\partial N} = -H^0(N)\,\psi^0(N), \qquad \psi^0(0) = \frac{R_{\rm i}}{v_{\rm p}} \qquad (17)$$

Using eq 13, we can formally write the solution as

$$\frac{\psi^0(N)}{\psi^0(0)} = \exp\left\{-\frac{1}{v_{\rm p}}\int_0^N H^0\right\} = \begin{cases} \exp\{-(\psi^0{}_l/v_{\rm p})\int_0^N k(N)\}, & N < n_0^* \\ [\psi^0(n_0^*)/\psi^0(0)]\exp\{-(H_s^0/v_{\rm p})N\}, & N > n_0^* \end{cases} \qquad (18)$$

But the long chain expression has almost all of the normalization of ψ^0, since $n_0^* \ll \bar{N}$, and thus this simple exponential form can be used to calculate $\bar{N}$ with small error. Thus

$$\bar{N} = \frac{v_{\rm p}}{H_s^0} \qquad (19)$$

Now an important general relation is that the net termination rate in a certain N range is proportional to the drop in ψ^0, as can be seen by integrating eq 17:

$$\psi^0(N_1) - \psi^0(N_2) = \frac{1}{v_{\rm p}}\int_{N_1}^{N_2} H^0\psi^0 \qquad (20)$$

It follows from eqs 20 and 15 that $R_{\rm term}^{\rm short}$ and $R_{\rm term}^{\rm long}$ are proportional to the drop in ψ^0 over the intervals $0 \rightarrow n_0^*$ and $n_0^* \rightarrow \infty$, respectively. Hence, eq 16 implies $\psi^0(n_0^*) = \psi^0(0)/2$, which, together with eq 18, immediately leads to an explicit expression for the total number of living chains:

$$\psi_l^0 = \frac{v_{\rm p}\ln 2}{\int_0^{\infty} k} \qquad (21)$$

We used $\int_0^{n_0^*} \approx \int_0^{\infty} k$ since $\int_0^N k$ converges for upper limit N of order z. Thus, using eqs 15, 16, 19, and 21, we have

$$\bar{N} = \frac{v_{\rm p}}{H_s^0} = \frac{2\psi_l^0 v_{\rm p}}{R_{\rm i}} = \frac{v_{\rm p}{}^2 2\ln 2}{R_{\rm i}\int_0^{\infty} k} \qquad (22)$$

Having determined ψ_l^0, the short chain MWD can be explicitly written as

$$\frac{\psi^0(N)}{\psi^0(0)} = \exp\left\{\frac{-\ln 2\int_0^N k}{\int_0^{\infty} k}\right\} = \begin{cases} \exp\{-C(N/z)^{1-\theta}\}, & N < z \\ \frac{1}{2}\exp\{(z/N)^{1/2}\}, & z < N < n_0^* \end{cases} \qquad (23)$$

where $\theta < 1$ is the $N < z$ reaction exponent, eq 2, and C is a constant of order unity. For $z < N < n_0^*$, where $k \sim 1/N^{3/2}$, the integral of k has almost converged and ψ^0 decays very slowly; we refer to this as the plateau region. For large N we have a simple exponential,

$$\frac{\psi^0(N)}{\psi^0(0)} = \frac{1}{2}\,{\rm e}^{-N/\bar{N}} \qquad (N > n_0^*) \qquad (24)$$

Let us summarize the steady state MWD as follows. For $N < n_0^*$ the MWD has one characteristic scale only, z, and varies as

$$\frac{\psi^0(N)}{\psi^0(0)} = g(N/z) \qquad (N < n_0^*) \qquad (25)$$

where the scaling function g has the following asymptotic behavior:

$$g(u) \approx \begin{cases} 1 - ({\rm const})u^{1-\theta}, & u \ll 1 \\ \frac{1}{2}(1 + u^{-1/2}), & u \gg 1 \end{cases} \qquad (26)$$

The short–long field dividing line, n_0^*, is not a scale in this regime; rather, it is a cutoff to the plateau behavior for $N \gg z$ at the point where the plateau slope first drops to the value of the slope of the large N exponential form of eq 24. This happens when $u = n_0^*/z = (\bar{N}/z)^{2/3} \gg 1$, i.e., well into the tail of $g(u)$. Note that ψ^0 has infinite

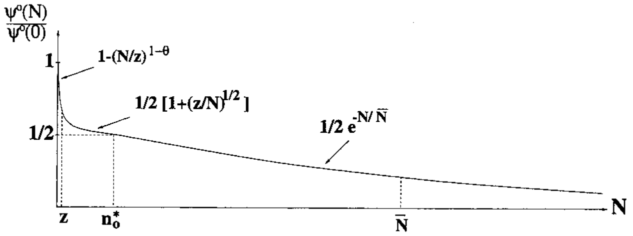

Figure 3. Theoretical steady state living chain molecular weight distribution (MWD), $\psi^0(N)$, for strongly entangled living chain population. Two subpopulations are identified: "short" chains, $N \lesssim z$, and "long" chains $N \gg z$. The characteristic short chain length, z, is the threshold length above which termination kinetics are dominated by entanglements. For small N, there is only one characteristic scale in ψ^0, namely z; the $N > z$ behavior in this region is a power law decay (the "plateau" region) asymptoting a value equal to exactly one half of the value at $N = 0$. This decay is cutoff at $N = n_0^* \gg z$. For $N > n_0^*$ the distribution is a simple exponential containing almost all of the normalization, $\bar{N} \gg n_0^* \gg z$: almost all living chains are long. The scale n_0^* separates the small and large N forms of the reaction field $H(N)$.

slope at the origin, unless $\theta = 0$. For $N > n_0^*$ the MWD has one scale only, $\bar{N}$ (eq 24). The steady state MWD is sketched in Figure 3.

We remark that in reality there are several $N < z$ regimes in ψ^0, each with a different $\theta < 1$ corresponding to the different $N < z$ regimes in k (see remarks following eq 2). To ease presentation, we have discussed a single regime only. The essential conclusions of this and later sections are insensitive to this simplification.

III. Posteffect Decay: Short and Intermediate Times, $t < \tau_{\mathrm{rad}}$

We consider a bulk FRP that has been run for long enough to reach the entanglement-dominated steady state regime studied in section II. Suddenly, at $t = 0$, the steady state is interrupted by switching off the driving force, $R_i \to 0$. How does $\psi_1(t)$ decay? What happens to the living MWD $\psi(N,t)$?

Now for $t > 0$ new macroradicals are not being created, but all living chains are growing with "velocity" v_p. Thus the entire MWD, initially ψ^0, is translating in the $+N$ direction with velocity v_p; the smallest living chain has length v_pt. Three characteristic time scales are naturally suggested:

$$\tau_{\mathrm{short}} \equiv \frac{z}{v_p}, \qquad \tau_{n_0^*} \equiv \frac{n_0^*}{v_p}, \qquad \tau_{\mathrm{rad}} \equiv \frac{\bar{N}}{v_p} = \frac{1}{H_s^0} \tag{27}$$

We have already met τ_{rad}, the lifetime of living chains in steady state. τ_{short} is a characteristic short chain time.

In this section we treat times much less than τ_{rad}. The distinguishing feature of this regime is that the MWD has shifted a distance much less than its width. In addition to this translation, there is of course termination whose magnitude we will now determine.

Now the time-dependent MWD $\psi(N,t)$ obeys

$$\frac{\partial\psi(N,t)}{\partial t} = -v_p\frac{\partial\psi(N,t)}{\partial N} - H(N,t)\,\psi(N,t),$$
$$\psi(0,t) = 0;\quad \psi(N,0) = \psi^0(N) \tag{28}$$

The boundary condition at $N = 0$ corresponds to zero radical source. The reaction field is now time-dependent:

$$H(N,t) = \int_{v_pt}^{\infty} \mathrm{d}M\, k(N,M)\, \psi(M,t) \approx \begin{cases} k(N)\,\psi_1(t) \approx k(N)\psi^0_{\ 1}, & N < n_t^* \\ \int_{v_pt}^{\infty} \mathrm{d}M\, k(M)\, \psi(M,t) \equiv H_s(t), & N > n_t^* \end{cases} \tag{29}$$

Just as in steady state, we find that H has relatively simple forms for small and large N values, respectively, relative to a time-dependent scale n_t^* (discussed below). These asymptotic forms are derived in detail in Appendix A, but their origin can be understood from the following simple considerations. Now in the integral defining $H(N,t)$ the integrand becomes negligibly small for M values much bigger than $\bar{N}$, this being the width of ψ (the assertion that this remains true for $t > 0$ will be self-consistently justified later in this section). Now consider a value $N \ll \bar{N}$; then for most relevant M values one may replace $k(N,M) \to K(N)$. The integral thus gives $k(N)\ \psi_1(t)$ plus corrections due to $M > N$ values whose smallness is quantified in Appendix A. But we will show below that the terminated fraction is always tiny; hence one may replace $\psi_1(t) \approx \psi_1^0$. Now consider a value N that is much greater than the maximum of z and v_pt. Then the contribution from all those M values that are less than N, for which $k(N,M) \approx k(M)$, is approximately equal to $H_s(t)$, as defined in eq 29. This is true to within small errors provided $t < \tau_{\mathrm{rad}}$, because the effective width of k is the larger of z or v_pt (see eqs 7 and 8 and associated discussion) both of which are much less than $\bar{N}$. Corrections due to $M > N$ are evaluated in Appendix A.

The short field–long field dividing line n_t^* obeys

$$k(n_t^*)\psi_1^0 = H_s(t) \tag{30}$$

and thus depends on the precise form of $H_s(t)$, which will be derived below. We will show that

$$n_t^* \approx n_0^* \qquad (t < \tau_{\mathrm{short}})$$

$$n_t^* \approx n_0^*\left(\frac{t}{\tau_{\mathrm{short}}}\right)^{1/3} = \bar{N}\left(\frac{t}{\tau_{\mathrm{rad}}}\right)^{1/3} = v_pt\left(\frac{\tau_{\mathrm{rad}}}{t}\right)^{2/3}$$
$$(\tau_{\mathrm{short}} < t < \tau_{\mathrm{rad}}) \tag{31}$$

Equation 31 tells us that the short–long domination of termination events persists provided $t < \tau_{\mathrm{rad}}$, since only then is n_t^* much less than the width $\bar{N}$ of the MWD. Note that, for $t > \tau_{\mathrm{short}}$, n_t^* moves in the $+N$ direction with velocity $(\mathrm{d}n_t^*/\mathrm{d}t) \approx v_p(\tau_{\mathrm{rad}}/t)^{2/3}$. For $t < \tau_{\mathrm{rad}}$ this is greater than v_p, which is the speed of growth of any given macroradical. Thus a macroradical initially shorter than n_t^* always experiences the short chain field, $k(N)\ \psi_1^0$. In contrast, a macroradical initially of length N greater than n_t^* gets "caught" at some time before τ_{rad} (unless $N \gg \bar{N}$) at which point its field, initially $H_s(t)$, will switch to the short form $k(N)\psi_1^0$ and remain so thereafter.

The long and short forms of H in eq 29 represent continuation of short-long domination into posteffect. The short field is again proportional to the number of long chains present, which approximates the entire population $\psi_1(t)$ (provided $n_t^* \ll \bar{N}$), while the integral defining the long field $H_s(t)$ is dominated by short chains, i.e., by N of order z if $t > \tau_{\mathrm{short}}$ and of order $v_{\mathrm{p}}t$ if $t > \tau_{\mathrm{short}}$. Short−long domination is manifest from the equality, as in steady state (see eq 15), of the total termination rates of short and long chains, respectively, which follows because z, $v_{\mathrm{p}}t \ll n_t^* \ll \bar{N}$:

$$R_{\mathrm{term}}^{\mathrm{short}} \equiv \int_{v_{\mathrm{p}}t}^{n_t^*} H\psi = \psi_{\mathrm{l}}(t) \int_{n_t^*}^{v_{\mathrm{p}}t} k\psi \approx H_{\mathrm{s}}(t)\, \psi_{\mathrm{l}}(t),$$

$$R_{\mathrm{term}}^{\mathrm{long}} \equiv \int_{n_t^*}^{\infty} H\psi \approx H_{\mathrm{s}}(t)\, \psi_{\mathrm{l}}(t) \quad (32)$$

Thus $R_{\mathrm{term}}^{\mathrm{short}} = R_{\mathrm{term}}^{\mathrm{long}}$ and the total termination rate, the sum of these two, equals $2H_{\mathrm{s}}(t)\, \psi_{\mathrm{l}}(t)$. Integrating the dynamical equation obeyed by ψ, eq 28, over all N values, one obtains

$$\frac{\mathrm{d}\psi_{\mathrm{l}}}{\mathrm{d}t} = -2H_{\mathrm{s}}(t)\, \psi_{\mathrm{l}}(t) \approx -2H_{\mathrm{s}}(t)\psi_{\mathrm{l}}^{0} \qquad (t < \tau_{\mathrm{rad}}) \qquad (33)$$

This is our basic dynamical equation for $\psi_{\mathrm{l}}(t)$. These dynamics are in general complex since $H_{\mathrm{s}}(t)$ is a functional of $[\psi]$. However, we will establish simple asymptotic forms for $H_{\mathrm{s}}(t)$, which considerably ease the task.

We will also aim to establish the posteffect living MWD. It is simple to show by direct substitution that a solution to eq 28 can be written

$$\psi(N,t) = \Theta(N - v_{\mathrm{p}}t)\, \psi^{0}(N - v_{\mathrm{p}}t)\mathrm{e}^{-\int_0^t \mathrm{d}t' H(N - v_{\mathrm{p}}[t-t'],t')} \qquad (34)$$

where $\Theta(x)$ is the step function. Thus in the extreme case that the posteffect field vanishes, $H = 0$, one would have $\psi(N,t) = \psi^{0}(N - v_{\mathrm{p}}t)$, which is the steady state MWD translating without termination. In the other limit, were the posteffect field to be undiminished from its steady state value, $H = H^{0}(N)$, then eq 34 would yield $\psi(N,t) = \Theta(N - v_{\mathrm{p}}t)\, \psi^{0}(N)$ after using eq 18. In what follows we will see that $\psi(N,t)$ has forms, in different domains of t and N, that approximate these two limits.

A. Shortest Times, $t < \tau_{\mathrm{short}}$: Behavior Unchanged from Steady State. For times t greater than τ_{short}, any short chain ($N \lesssim z$) if unterminated will have grown to become long ($N > z$). On the other hand in the earliest regime, $t < \tau_{\mathrm{short}}$, the identity of short and long chains deviates little from steady state where we have seen in section II that short−long terminations dominate. One might expect, therefore, that the situation in posteffect would be essentially unchanged from steady state for these times. This we will now demonstrate.

Consider $t < \tau_{\mathrm{short}}$. Now from eq 29 the short chain field is the same as in steady state for all $N < n_t^* \approx n_0^*$. Setting $H = H^{0}$ in eq 34, one has $\psi = \Theta(N - v_{\mathrm{p}}t)\, \psi^{0}(N)$ for $N \lesssim n_0^*$. Thus, in the expression for the long chain field $H_{\mathrm{s}}(t)$, eq 29, one may replace ψ with ψ^{0} since this integral is dominated by M values of order z and much less than n_0^*. Thus

$$H_{\mathrm{s}}(t) \approx \int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}N\, k(N)\, \psi^{0}(N) \qquad (t < \tau_{\mathrm{short}}) \qquad (35)$$

For these times, the crucial point is that the lower limit $v_{\mathrm{p}}t$ is much less than z, which is the N value dominating the integral. Hence the integral is very close to its value with the lower limit set to zero, namely the steady state value H_{s}^{0}. Indeed, using the $N < z$ form for ψ^{0} (eq 23) and using $k(N{<}z) = k(z)\, (z/N)^{\theta}$ (eq 2) one sees that the relative contribution to the integral from $N < v_{\mathrm{p}}t$ is indeed small:

$$\frac{\int_0^{v_{\mathrm{p}}t} k\psi^{0}}{\int_0^{\infty} k\psi^{0}} \approx \frac{\psi^{0}(0)\int_0^{v_{\mathrm{p}}t} k}{k(z)\, \psi^{0}(0)z} \approx \left(\frac{t}{\tau_{\mathrm{short}}}\right)^{1-\theta} \qquad (t < \tau_{\mathrm{short}}) \quad (36)$$

This leads to

$$H_{\mathrm{s}}(t) = H_{\mathrm{s}}^{0} \left\{1 - \left(\frac{t}{\tau_{\mathrm{short}}}\right)^{1-\theta}\right\} \qquad (t < \tau_{\mathrm{short}}) \quad (37)$$

Thus, the reaction field $H_{\mathrm{s}}(t)$ on long chains, $N > n_0^*$, is very close to its steady state value. Note that the validity of this conclusion relies on $\theta < 1$.

Thus we have established that the entire reaction field is the same as in steady state, plus small corrections. This confirms $n_t^* \approx n_0^*$, which was asserted in eq 31 and allows one to set the reaction field to its steady state value for *all* N in eq 34, $H \rightarrow H^{0}$. We conclude that the MWD is just the steady state one with the $N < v_{\mathrm{p}}t$ part missing:

$$\psi(N,t) = \Theta(N - v_{\mathrm{p}}t)\, \psi^{0}(N) \qquad (t < \tau_{\mathrm{short}}) \qquad (38)$$

Having found that the long chain field $H_{\mathrm{s}}(t)$ is essentially unchanged from steady state, let us use the kinetics of eq 33 to deduce the number of living chains that have terminated after time t. Recalling that $H_{\mathrm{s}}^{0} = 1/\tau_{\mathrm{rad}}$ and using eqs 15, 22, and 16, one finds

$$-\Delta\psi_{\mathrm{l}} \approx \psi_{\mathrm{l}}^{0}\frac{2t}{\tau_{\mathrm{rad}}} = R_{\mathrm{i}}t \qquad (39)$$

The termination rate is unchanged from its steady state value. By the end of this regime, $t = \tau_{\mathrm{short}}$, a small fraction $z/\bar{N}$ of the living population has disappeared.

Figure 4a illustrates the short time living MWD of eq 38. Note that the area of the missing $N < v_{\mathrm{p}}t$ part equals $\psi^{0}(0)\ v_{\mathrm{p}}t$ plus small corrections, since ψ^{0} has decreased little, for $N \ll z$, from its $N = 0$ value. Then, using the boundary condition of eq 17, one sees that this area equals $R_{\mathrm{i}}t$, in accordance with eq 39.

B. Intermediate Times, $\tau_{\mathrm{short}} < t < \tau_{\mathrm{rad}}$: Disappearance of Short Chains. For $t > \tau_{\mathrm{short}}$ the entire short population has disappeared. Any short chain that has not terminated will have grown to become long. Consequently, the kinetics of steady state must have been completely destroyed by this time. We will see that the long chain reaction field $H_{\mathrm{s}}(t)$, which in steady state was dominated by short chains, is now drastically diminished.

To calculate $H_{\mathrm{s}}(t)$ using eq 29, we must first determine the living MWD ψ. This is done in Appendix B. Consider firstly the MWD for times $\tau_{\mathrm{short}} < t < \tau_{n_0^*}$, as shown in Figure 4b (see eqs B2 and B3). For $N < n_0^*$, ψ is the steady state MWD with the $N < v_{\mathrm{p}}t$ part missing, $\psi = \Theta(N - v_{\mathrm{p}}t)\psi^{0}$; by these times most of the short population of ψ^{0} has disappeared, including those N of order z that dominated the steady state H_{s}^{0}. For large $N \gg n_0^*$, ψ is the *translating* steady state MWD, $\psi = \psi^{0}(N - v_{\mathrm{p}}t)$. Between these two regions there is a very flat "extended plateau region" of size of order $v_{\mathrm{p}}t$. Indicated on the figure is the region named ABDC whose area (as explained in the caption) is equal to the number of terminated living chains. Observing that the

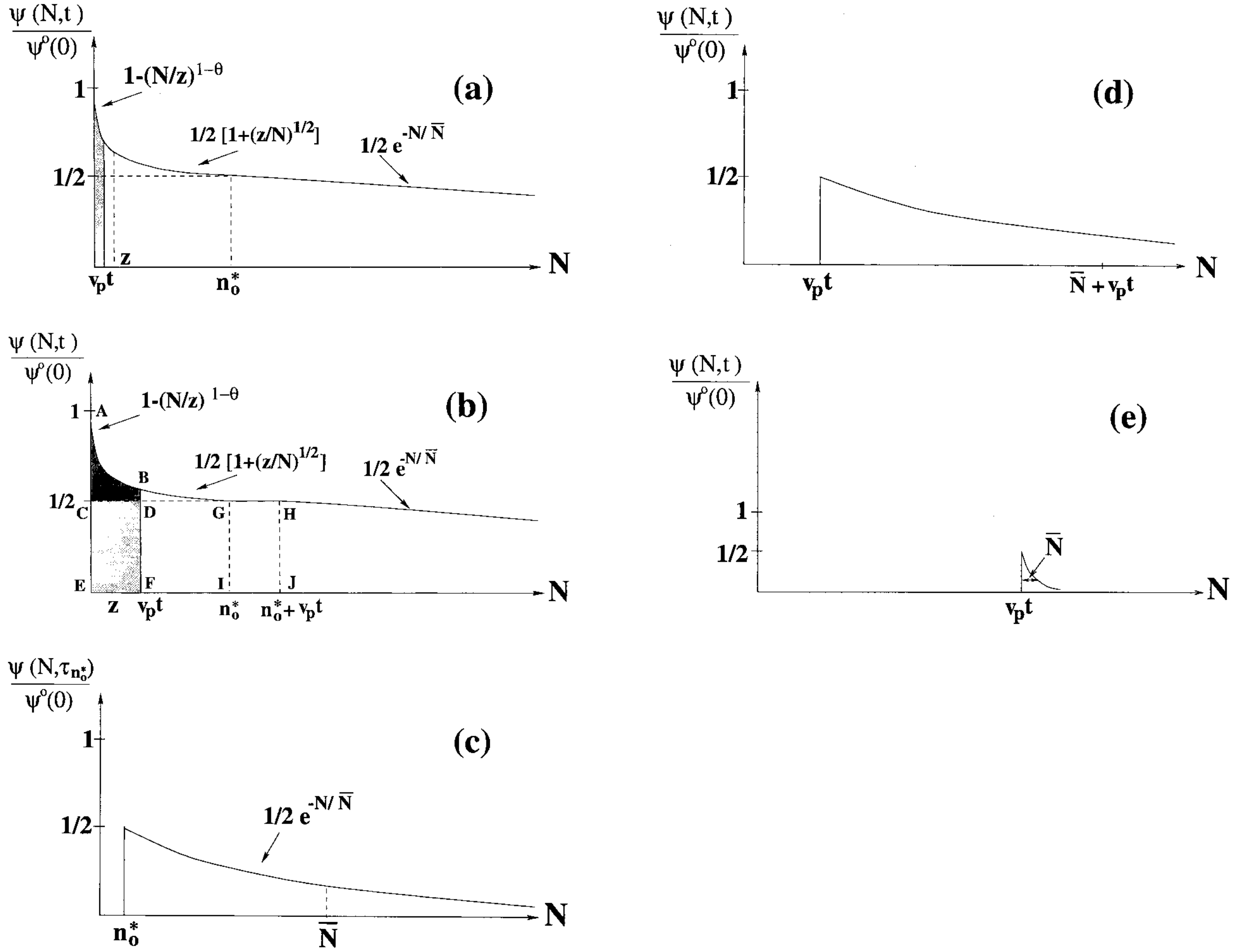

Figure 4. Posteffect living MWD at various times t after radical production has been switched off (entanglement-dominated termination). (a) $t \ll \tau_{\text{short}}$. Other than the missing shaded part ($N < v_{\text{p}}t$) the MWD is essentially unchanged from steady state. These missing short chains are a small fraction of the short population. Thus the long chain field, and hence the net termination rate, is little changed from steady state. (b) $\tau_{\text{short}} \ll t \ll \tau_{n_0^*}$. The short chains (chains of length of order z or less) have disappeared (shaded). Thus the long chain reaction field (dominated in steady state by short chains) and overall termination rate are greatly diminished. ψ coincides with the steady state MWD ψ^0 along BG and, approximately, to the right of H (here ψ is approximately ψ^0 shifted by $v_{\text{p}}t$), while GH is approximately flat. Thus the missing area under ψ (relative to ψ^0) is ABFE − GHJI ≈ ABDC (dark-shaded region). The area of ABDC is estimated in eq 40. (c) $t = \tau_{n_0^*}$. Only the long chain exponential part of ψ remains, $\psi \approx (1/2) \exp\{-(N - n_0^*)/\bar{N}\}$. (d) $\tau_{n_0^*} < t < \tau_{\text{rad}}$. The MWD of (c) simply translates in the $+N$ direction with velocity v_{p} and negligible termination (because no short chains exist). (e) $t \gg \tau_{\text{rad}}$. The MWD moves further and further to the right. By these times, it has shifted a distance much greater than its width, $\bar{N}$, and has thus become approximately *monodisperse* with mean chain length $\approx v_{\text{p}}t$.

dominant contributions are from $N > z$, where ψ^0 has the plateau form of eqs 25 and 26, one finds that the area is approximately given by

$$-\Delta\psi_1 \approx \int_0^{v_{\text{p}}t} \mathrm{d}N\,[\psi^0(N) - \psi^0(0)/2] \approx (\psi^0(0)/2) \int_0^{v_{\text{p}}t} \mathrm{d}N \left(\frac{z}{N}\right)^{1/2} \approx \left(\frac{z}{\bar{N}}\right)^{1/2} \left(\frac{t}{\tau_{\text{rad}}}\right)^{1/2} \psi_1^0 \tag{40}$$

We will see that this estimate of the missing area under ψ is in accord with the terminated fraction that will be calculated systematically below, using eq 33.

By the time $t = \tau_{n_0^*}$ the entire short chain population has disappeared, and the MWD is shown in Figure 4c. Essentially, this is the initial steady state MWD with the entire short part deleted (see eq B4). We show in Appendix B that for longer times the reaction field is so small, the short population having disappeared, that termination is negligible: the distribution essentially translates with speed v_{p},

$$\frac{\psi(N,t)}{\psi^0(0)} \approx \frac{1}{2}\mathrm{e}^{-(N-v_{\text{p}}t)/\bar{N}} \qquad (\tau_{n_0^*} < t < \tau_{\text{rad}}) \tag{41}$$

as depicted in Figure 4d.

It follows that for these times ψ is varying very slowly as a function of N since all the sharp $N \lesssim z$ features in ψ^0 have disappeared. Thus in the integral defining $H_{\text{s}}(t)$ of eq 29, k multiplies a slowly varying ψ of width $\bar{N}$ much greater than the effective width of k, namely the lower cut off $v_{\text{p}}t$. Thus k picks out ψ evaluated at $N \approx v_{\text{p}}t$ (see eq 8) and the reaction field scales as the integral of k. This is demonstrated explicitly in Appendix C,

$$H_{\text{s}}(t) = \int_{v_{\text{p}}t}^{\infty} k\psi = \psi(v_{\text{p}}t,t) \int_{v_{\text{p}}t}^{\infty} \mathrm{d}N\, k(N)[1 + O(\tau_{\text{short}}/t)^{1/2} + O(t/\tau_{\text{rad}})^{1/2}]$$

$$= \frac{\psi^0(0)}{2} \int_{v_p t}^{\infty} \mathrm{d}N\, k(N)[1 + O(\tau_{\mathrm{short}}/t)^{1/2} + O(t/\tau_{\mathrm{rad}})^{1/2}] \qquad (\tau_{\mathrm{short}} < t < \tau_{\mathrm{rad}}) \quad (42)$$

We have used eqs B2, 25, and 26 to replace $\psi(v_p t,t)$ with $\psi^0(0)/2$ to within the stated errors. Thus, since $k \sim 1/N^{3/2}$, we have

$$H_s(t) \approx H_s^0 \left(\frac{\tau_{\mathrm{short}}}{t}\right)^{1/2} \qquad (43)$$

after making use of eq 13. The leading relative corrections to the above result are order $(\tau_{\mathrm{short}}/t)^{1/2}$ and $(t/\tau_{\mathrm{rad}})^{1/2}$.

We have found that the reaction field $H_s(t)$ decays as $1/t^{1/2}$. This confirms our expectation that $H_s(t)$ has dropped drastically below its steady state value and immediately confirms the expressions for n_t^* in eq 31 after using the definition of eq 30. Inserting this into the $\psi_l(t)$ kinetics, eq 33, we finally obtain our expression for the terminated fraction during the intermediate regime:

$$\frac{-\Delta\psi_l}{\psi_l^0} \approx \left(\frac{z}{\bar{N}}\right)^{1/2} \left(\frac{t}{\tau_{\mathrm{rad}}}\right)^{1/2} \qquad (44)$$

plus relative corrections of order $(\tau_{\mathrm{short}}/t)^{1/2}$ and $(t/\tau_{\mathrm{rad}})^{1/2}$. This is one of the principal predictions of the present study: the terminated fraction increases like $t^{1/2}$ during the intermediate regime. We will compare with experiment in the final section.

IV. Posteffect Decay: Long Times, $t > \tau_{\mathrm{rad}}$

In the previous section we saw that for $\tau_{n_0^*} < t < \tau_{\mathrm{rad}}$ the living MWD is approximately the long chain part of the initial steady state distribution, translating with speed v_p. Thus the width of ψ is $\bar{N}$, as in steady state. By the time τ_{rad}, when the MWD has translated an amount equal to its width, according to eq 44 the fractional termination is very small:

$$\frac{-\Delta\psi_l(\tau_{\mathrm{rad}})}{\psi_l^0} \approx \left(\frac{z}{\bar{N}}\right)^{1/2} \ll 1 \qquad (45)$$

Since the reaction field H is monotonically decreasing in time, it follows that the lifetime of the living population must be *much greater than the steady state value* τ_{rad}: the MWD translates many times its own width before being substantially diminished by termination. This, in turn, implies that the MWD is becoming *increasingly monodisperse* as the chains continue to grow with little termination; for times $t \gg \tau_{\mathrm{rad}}$, the mean living chain length is approximately $v_p t$ and is much greater than the spread in lengths, $\bar{N}$. This is depicted in Figure 4e.

It follows that the termination rate constant between any living pair is approximately independent of chain length, $k(N,M) \approx k(v_p t, v_p t)$. This greatly simplifies the expression for the total termination rate:

$$\frac{\mathrm{d}\psi_l}{\mathrm{d}t} = -\int_0^{\infty} \mathrm{d}M \int_0^{\infty} \mathrm{d}N\, k(N,M)\, \psi(M,t)\, \psi(N,t)$$

$$\approx -k(v_p t, v_p t){\psi_l}^2 \left\{1 + O\left(\frac{\tau_{\mathrm{rad}}}{t}\right)\right\} \qquad (t \gg \tau_{\mathrm{rad}}) \quad (46)$$

This result and the correction term are derived systematically in appendix D. Evidently, we recover the "Flory theory" of FRP, which ignores the chain-length dependence of k, but with one essential difference: the rate constant is now effectively time dependent, being evaluated at the current mean living chain length, $v_p t$,

$$k(v_p t, v_p t) \approx k(z) \left(\frac{\tau_{\mathrm{short}}}{t}\right)^{3/2} \qquad (47)$$

This follows because $k(N,N)$ scales identically to $k(N)$ (see eq 2). Equation 46 is immediately solved, giving

$$\frac{\psi_l(t)}{\psi_l^0} = [\psi_l^0 \int_{\tau_{\mathrm{rad}}}^{t} \mathrm{d}t\, k(v_p t, v_p t) + [\psi_l^0/\psi_l(\tau_{\mathrm{rad}})]]^{-1} \qquad (48)$$

where we have taken our initial condition at $t = \tau_{\mathrm{rad}}$, roughly the time at which this regime begins. Now from the preceding regime (see eq 45) we have $\psi_l(\tau_{\mathrm{rad}})/\psi_l^0 \approx 1 - (z/\bar{N})^{1/2}$, while eq 47 with the help of eqs 21 and 7 leads to

$$\psi_l^0 \int_{\tau_{\mathrm{rad}}}^{t} \mathrm{d}t\, k(v_p t, v_p t) \approx \left(\frac{z}{\bar{N}}\right)^{1/2} - \left(\frac{\tau_{\mathrm{short}}}{t}\right)^{1/2} \qquad (t \gg \tau_{\mathrm{rad}}) \quad (49)$$

Expanding eq 48 to leading order in the small quantities $(z/\bar{N})$ and τ_{short}/t, one obtains for the long time reacted fraction

$$\frac{-\Delta\psi_l(t)}{\psi_l^0} \approx \left(\frac{z}{\bar{N}}\right)^{1/2} \left\{2 - \left(\frac{\tau_{\mathrm{rad}}}{t}\right)^{1/2}\right\} \qquad (t \gg \tau_{\mathrm{rad}}) \quad (50)$$

We see that the reacted fraction approaches a finite and small value, approximately $(z/\bar{N})^{1/2}$, as $t \to \infty$. This approach follows a $t^{-1/2}$ law. That is, the living population *never* decays to zero, a direct result of the convergence of the integral in eq 48 as $t \to \infty$. This, in turn, was a consequence of the fact that $k(N)$ decays faster than $1/N$.

The infinite lifetime is the second principal prediction of our theory. The complete posteffect evolution of the terminated fraction is shown in Figure 5.

V. Summary and Comparison with Experiment

The physical picture emerging from this work is summarized schematically in Figure 6. When a FRP is run in steady state, the conversion ϕ gradually increases, causing the mean living chain length $\bar{N}$ to increase. But the entanglement threshold, z, is a *decreasing* function of ϕ (theory predicts[17,31] $z \sim \phi^{-\omega}$ with $\omega \approx 1$). At sufficiently high conversions, therefore, the great majority of living chains become strongly entangled in their dead chain surroundings: $\bar{N} \gg z$ and almost all living chains are long, $N > z$. A small fraction, $z/\bar{N}$, are short, $N < z$. The total termination rate, $R_{\mathrm{term}}^{\mathrm{total}} \approx k(z)\psi_s^0\, \psi_l^0$ (see eqs 13 and 15) is dominated by short−long reactions (see Figure 6a).

In posteffect experiments, R_i is suddenly set to zero at $t = 0$ when the situation of Figure 6a pertains. During the first regime, $0 < t < \tau_{\mathrm{short}}$, the long chain population is negligibly affected. Thus the short chain field is negligibly changed from steady state. But, under

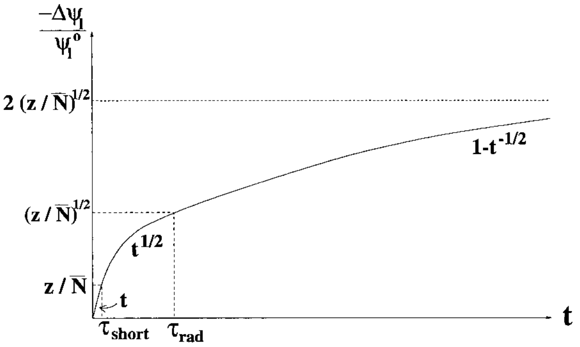

Figure 5. Entangled FRPs. Predicted evolution of the fraction of living chains that have terminated after time t, $-\Delta\psi_1(t)/\psi_1^0$. During the initial linear regime the constant termination rate equals the steady state value. By $t = \tau_{\rm short}$ the short chain population (a fraction $z/\bar{N}$ of the entire living population) has disappeared. Then a $t^{1/2}$ regime commences until $\tau_{\rm rad}$ (the steady state living chain lifetime). For $t > \tau_{\rm rad}$ the termination rate drops so rapidly that the net fractional termination saturates at a value $\approx(z/\bar{N})^{1/2}$.

the action of this field, the mean short chain survival time before termination is of order $\tau_{\rm short}$ since in the interval $0 < N < z$ the steady state MWD drops by a factor of order unity (see Figure 3). Hence a fraction of order unity of the short chains terminate by $t = \tau_{\rm short}$; i.e. a fraction $z/\bar{N}$ of the living population has terminated by that time.

For $t > \tau_{\rm short}$ the termination rate is massively reduced from the steady state value since the mobile short chains no longer exist: any short chain avoiding termination has had time to grow to become long (Figure 6b). Nonetheless, short−long domination persists. But now "short" means a length equal to $v_{\rm p}t$ to within a prefactor of order unity. For $t < \tau_{\rm rad}$, the number of such short chains is approximately a fraction $(v_{\rm p}t/\bar{N})$ of the total living population, since the MWD is broad. Thus the net termination rate is decaying as $t^{-1/2}$: $R_{\rm term}^{\rm total}(t) \approx k(v_{\rm p}t)(v_{\rm p}t/\bar{N})(\psi_1^0)^2 \approx (\tau_{\rm short}/t)^{1/2}R_{\rm term}^{\rm total}(0)$ where $R_{\rm term}^{\rm total}(0)$ is the steady state value. Hence the terminated fraction, the time integral of $R_{\rm term}^{\rm total}(t)$, increases as $t^{1/2}$. By the end of this intermediate regime, $\tau_{\rm short} < t < \tau_{\rm rad}$, only a very small fraction $\approx(z/\bar{N})^{1/2}$ of the living population has terminated (see Figure 5).

The final regime, $t > \tau_{\rm rad}$, is depicted in Figure 6c. The mean chain length $v_{\rm p}t$ is now much greater than the variation in length, of order $\bar{N}$. Thus, the short−long mechanism is no longer relevant and termination kinetics are now approximately monodisperse, $R_{\rm term}^{\rm total}(t) \approx k(v_{\rm p}t,v_{\rm p}t)\psi_1{}^2$. The time-dependent rate constant, $k(v_{\rm p}t,v_{\rm p}t) \sim 1/t^{3/2}$, decays too rapidly for the living population to be able to terminate itself: as $t \to \infty$, so the terminated fraction saturates at a small value of order $(z/\bar{N})^{1/2}$ (see eq 50). This is the final phase in Figure 5.

How do these predictions compare with experiment? The ESR measurements of Zhu et al.[11] shown in Figure 1 are clearly in qualitative agreement: above conversions of $\phi \approx 20\%$, where the FRPs are entangled, the living chain population achieves only partial decay. In our picture, this partial decay corresponds to the disappearance of the short chains that existed at $t = 0$ (plus the few long chains with which they terminated), followed by the disappearance of a fraction $(z/\bar{N})^{1/2}$ of longer chains (the intermediate $t^{1/2}$ behavior). A significant feature of the experimental curves is that the fraction which ultimately terminates is a decreasing function of conversion; this is consistent with our theory, since $(z/\bar{N})^{1/2}$ decreases[17] with increasing ϕ. At the

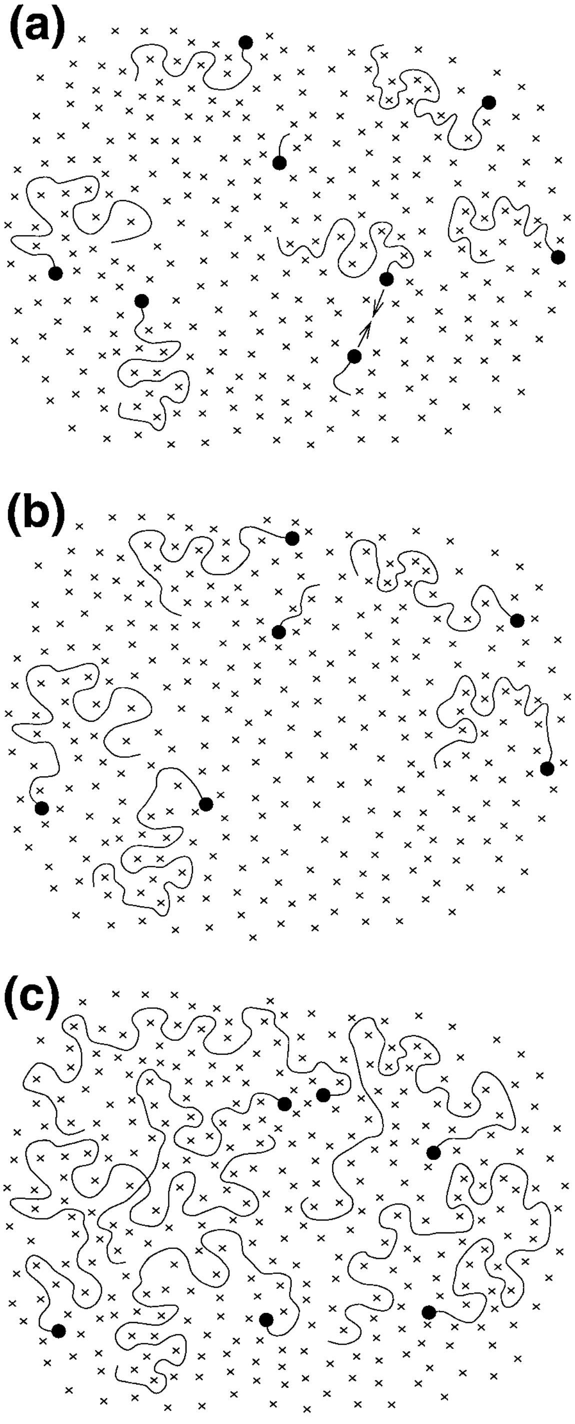

Figure 6. Schematic of living chain population during post-effect. Entanglement constraints of dead chain background are shown as crosses. (a) $t = 0$. In steady state, though almost all chains are long (entangled) a small fraction are short (unentangled). These are so much more mobile that short−long termination reactions are dominant. (b) $\tau_{\rm short} < t < \tau_{\rm rad}$. The short chains have all either terminated or grown to become long. Termination can now only be achieved through reaction of two long low-mobility living chains and is thus strongly suppressed relative to steady state. (c) $t \gg \tau_{\rm rad}$. All chains are much longer than the mean length in (a), $\bar{N}$. Chain lengths are increasing linearly in time, $\mathrm{d}N/\mathrm{d}t = v_{\rm p}$. The decay of rate constants with increasing chain length, $k \sim 1/N^{3/2}$, is so rapid that the living chain population can never terminate itself: lifetimes are infinite.

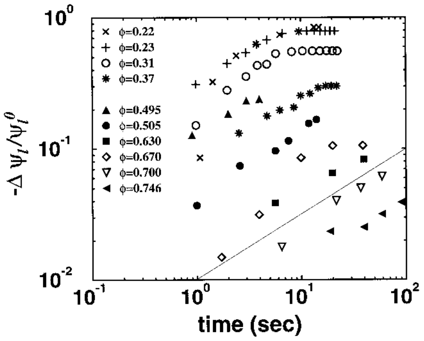

Figure 7. Logarithmic plots of the terminated fraction, $-\Delta\psi_l/\psi_l^0$, versus time for two sets of ESR posteffect measurements on bulk FRPs. The symbols ×, +, ○, ∗ ($\phi = 0.22$, 0.23, 0.31, 0.37) label the data of Zhu et al.,[11] shown in Figure 2 of this paper. The other symbols ($\phi = 0.495$, 0.505, 0.63, 0.67, 0.7, 0.746) label the data of Shen et al., Figure 2 of ref 12: MMA at 26 °C, with 0.337 mol/L ultraviolet-initiated benzoyl peroxide. The solid line has slope $^1/_2$, as theoretically predicted for the "intermediate" time regime for entanglement-dominated FRPs.

highest conversion shown, $\phi = 0.78$, the FRP is presumably near a glass transition. A future paper will consider such situations.

A more quantitative comparison with theory is afforded by the logarithmically presented measurements shown in Figure 7. The terminated fraction, $-\Delta\psi_l/\psi_l^0$, is shown versus time for various conversions. The data of Figure 1 are included here for intermediate conversions, $0.22 \leq \phi \leq 0.37$, together with a second independently obtained set due to Shen et al.[12] All of these FRPs are entangled. The time domain in Figure 7 includes what our theory would identify as the "intermediate" regime. All sets of data exhibit a behavior that is approximately algebraic and rather close to the predicted $t^{1/2}$ behavior (shown as the solid line), followed by saturation.

Recalling that our $t^{1/2}$ prediction resulted from two integrations of the $k \sim 1/N^{3/2}$ prediction[31,32] for entangled reacting polymers, one sees that comparison of the data in Figure 7 with the solid theoretical line amounts to a test of this fundamental scaling law, which has hitherto been unavailable. More generally, if the scaling prediction had been $k \sim 1/N^{\alpha}$ (with $\alpha > 1$), then using $R_{\rm term}^{\rm total} \sim k(v_{\rm p}t)v_{\rm p}t$ one would have obtained $\Delta\psi_l(t) \sim \int_0^t R_{\rm term}^{\rm total} \sim t^{2-\alpha}$. This provides another motivation, beyond the principal one of improving our basic understanding of FRP, to perform more detailed and controlled future experiments that can scrutinize the detailed time dependence of posteffect living chain decay. The techniques of ESR[11-13,39-44] and, depending on the radical species, infrared and ultraviolet absorption[45,46] are powerful and versatile methods for this purpose.

Acknowledgment. This work was supported by the National Science Foundation under grant no. DMR-9403566. We thank Oleg Bychuk for helpful discussions.

Appendix A. Short and Long Chain Limits of Reaction Field for $t < \tau_{\rm rad}$

In this appendix we derive the asymptotic forms shown in eq 29 of the time-dependent posteffect reaction field $H(N,t)$ for very large and very small N, respectively. The reaction field is given by

$$H(N,t) = \int_{v_{\rm p}t}^{\infty} {\rm d}M\ k(N,M)\ \psi(M) \qquad \text{(A1)}$$

where the t entry in ψ is dropped to ease notation. We consider times $t < \tau_{\rm rad}$. Note that the minimum living chain length is $v_{\rm p}t$ and that ψ has width $\bar{N}$.

Now it was shown in ref 36 that $k(M,N)$ has the structure

$$k(N,M) = K(N)\ h(M/N), \qquad h(u \gg 1) = 1 + u^{-\eta} + ... \qquad \text{(A2)}$$

where the exponent $\eta \geq {}^1/_2$. The crossover function h quantifies result (3) of eq 2, which stated that $k(N) \equiv k(N,M{=}\infty)$ is dominated by the small chain, $N \ll M$. $h(u)$ is monotonically decreasing and is of order unity for u of order unity.

Consider first the large N behavior. We write

$$H(N,t) = H_{\rm s}(t) - X + Y + Z, \qquad H_{\rm s}(t) \equiv \int_{v_{\rm p}t}^{\infty} {\rm d}M\ k(M)\ \psi(M) \qquad \text{(A3)}$$

where the corrections to the term $H_{\rm s}(t)$, which we will see is dominant for large N, are given by

$$X \equiv \int_N^{\infty} {\rm d}M\ K(M)\ \psi(M) \approx Nk(N)\ \psi(N)$$

$$Y \equiv \int_N^{\infty} {\rm d}M\ K(N,M)\ \psi(M) = k(N) \int_N^{\infty} {\rm d}M\ f(M/N)\ \psi(M)$$

$$\approx k(N) \int_N^{\infty} {\rm d}M\ \psi(M) \approx k(N)\psi_l \qquad (N < \bar{N})$$

$$Z \equiv \int_{v_{\rm p}t}^{N} {\rm d}M\ [k(N,M) - k(M)]\psi(M) = \int_{v_{\rm p}t}^{N} {\rm d}M\ [f(N/M) - 1]k(M)\ \psi(M)$$

$$\approx \int_{v_{\rm p}t}^{N} {\rm d}M\ (M/N)^{\eta}\ k(M)\ \psi(M) \approx Nk(N)\ \psi(N) \qquad \text{(A4)}$$

Now we will see below that "large" N here means $N \gg z$. Thus the integral defining X is dominated by its lower limit since $k \sim 1/M^{3/2}$ throughout the range of integration. This leads to the estimate for X above. To estimate Y, we noted that $f(M/N) \approx 1$ for $M > N$ and we assumed $N < \bar{N}$; for $N > \bar{N}$ this correction term is much smaller. In estimating Z we have used $\eta \geq {}^1/_2$; for $\eta > {}^1/_2$ the integral defining Z is dominated by its upper limit $M = N$, while for $\eta = {}^1/_2$ an extra and unimportant logarithmic correction factor results, $\ln(N/v_{\rm p}t)$.

Thus for $N \ll \bar{N}$ the ratios $X/Y \approx Z/Y \approx Nk(N)\ \psi(N)/k(N)\psi_l^0 \approx N/\bar{N}$ are much less than unity and the dominant correction term is Y. Note that we can always replace $\psi_l(t) \rightarrow \psi_l^0$ to a very good approximation since it is shown in this paper that the fractional termination is much less than unity for all times.

Now in the main text it is shown (see eq 37) that $H_{\rm s}(t) \approx H_{\rm s}^0 \approx k(z)z\psi(z)$ for short times $t < \tau_{\rm short}$ (i.e., $v_{\rm p}t < z$). For longer times, $\tau_{\rm short} < t < \tau_{\rm rad}$, $H_{\rm s}(t) \approx H_{\rm s}^0(\tau_{\rm short}/t)^{1/2}$ (see eq 43). Thus for $t < \tau_{\rm short}$ the leading relative correction in eq A3 is $Y/H_{\rm s}(t) \approx k(N)\psi_l^0/k(z)z\psi(z) \approx k(N)\bar{N}/k(z)z = (n_0^*/N)^{3/2}$ using eq 14. Meanwhile, for $t > \tau_{\rm short}$ the correction is $Y/H_{\rm s}(t) \approx (n_0^*/N)^{3/2}(t/\tau_{\rm short})^{1/2} = (n_t^*/N)^{3/2}$ where $n_t^* \equiv n_0^*(t/\tau_{\rm short})^{1/3}$, as defined in eq 31.

Thus we can write

$$H(N,t) \approx H_s(t)\left\{1 + \text{const}\frac{k(N)\psi_1^0}{H_s(t)}\right\} \approx H_s(t)\left\{1 + \text{const}\left(\frac{n_t^*}{N}\right)^{3/2}\right\} \qquad (N < \bar{N}) \quad \text{(A5)}$$

with the full definition of n_t^* given by eq 31. We have thus shown that for $N \gg n_t^*$ the reaction field $H(\underline{N},t)$ is very well approximated by $H_s(t)$. For $N > \bar{N}$ the approximation is even better.

To treat small N, we now write the reaction field as

$$H(N,t) = k(N)\int_{v_pt}^{\infty}\psi - X' + Y' + Z' \qquad \text{(A6)}$$

where the first and dominant term (for small N) equals approximately $k(N)\psi_1^0$ (since $v_pt \ll \bar{N}$) and the corrections are given by

$$X' \equiv k(N)\int_{v_pt}^{N}\psi \approx k(N)[(N - v_pt)/\bar{N}]\psi_1^0$$

$$Y' \equiv \int_{v_pt}^{N} \mathrm{d}M\, K(N,M)\,\psi(M) = \int_{v_pt}^{N} \mathrm{d}M\, f(N/M)\, k(M)\,\psi(M)$$

$$\approx \int_{v_pt}^{N} \mathrm{d}M\, k(M)\,\psi(M) \approx H_s(t) \qquad (N \gg v_pt,\, z)$$

$$Z' \equiv \int_N^{\infty} \mathrm{d}M\,[k(N,M) - k(N)]\psi(M) = k(N)\int_N^{\infty} \mathrm{d}M\,[f(N/M) - 1]\psi(M)$$

$$\approx k(N)\int_N^{\infty} \mathrm{d}M\,(N/M)^{\eta}\psi(M) \approx k(N)\bar{N}(N/\bar{N})^{\eta}\psi(\bar{N}) \approx k(N)\psi_1^0(N/\bar{N})^{\eta} \qquad (\eta < 1) \quad \text{(A7)}$$

Here $Y' \approx H_s(t)$ holds provided the upper limit of the integral, N, exceeds the maximum of v_pt and z; the upper limit must exceed these values for the integral to have converged to $H_s(t)$ (see the discussion surrounding eqs 7 and 8). For smaller N values, Y' is even smaller than the above estimate. In estimating Z' we assumed $\eta >$ 1, which implied $\underline{\text{th}}$e integral was dominated by the cutoff in ψ at $M = \bar{N}$. If, instead, $\eta > 1$, then the lower integral limit dominates, giving $Z' \approx k(N)\psi_1^0(N\bar{N}) \approx X'$.

Thus we can write eq A6 as

$$H(N,t) = k(N)\,\psi_1(t)\left\{1 + \text{const}\left(\frac{N}{n_t^*}\right)^{3/2} + \text{const}\left(\frac{N}{\bar{N}}\right)^{\eta}\right\} \qquad (\eta < 1) \quad \text{(A8)}$$

where the first correction term, due to Y', is equal to $H_s(t)/k(N)\psi_1^0$. We have already calculated the inverse of this quantity in eq A5. The second correction term is due to Z'. For $\eta > 1$ this term is replaced by $N/\bar{N}$ and is equally contributed to by Z' and X'.

Equations A5 and A8 together have verified eq 29 of the main text. That is, $H \approx H_s(t)$ for $N > n_t^*$ and $H \approx k(N)\,\psi_1(t)$ for $N < n_t^*$.

Appendix B. Posteffect at Intermediate Times, $\tau_{\text{short}} < t < \tau_{\text{rad}}$: Calculation of MWD

In this appendix we determine the living MWD during the "intermediate" regime, $\tau_{\text{short}} < t < \tau_{\text{rad}}$. A helpful quantity will be the total termination probability of a given macroradical, which grows from, e.g., N_1 to $N_2 = N_1 + v_p(t_2 - t_1)$ in a time interval $t_1 \to t_2$. This can be expressed in terms of the full reaction field, $H(N,t)$, by solving eq 28 with initial condition $\psi(N,t_1) = \delta(N-N_1)$. Seeking a solution of the form $\psi(N,t) = S(t)\,\delta(N-[N_1+v_p(t-t_1)])$, where $S(t)$ is the survival probability, a solution for S is easily obtained. The termination probability is $1 - S$:

$$P^{\text{term}}(N_1 \rightarrow N_2, t_1 \rightarrow t_2) = 1 - \mathrm{e}^{-\int_{t_1}^{t_2}\mathrm{d}t' H(N_2 - v_p[t_2 - t'],t')} \approx \int_{t_1}^{t_2}\mathrm{d}t'\, H(N_2 - v_p[t_2 - t'],t') \quad \text{(B1)}$$

where we have expanded the exponential because the total termination probability turns out to be much less than unity for any time.

Consider shorter chains first. Now from eq 31 and the discussion following it, any living chain whose length at time t is less than $n_0^* + v_pt$ (i.e., whose length was initially less than n_0^*) must have been subjected to the short chain field always. For such chains we can thus set $H(N,t) = k(N)\psi_1^0$ in eq 34, which gives

$$\psi(N,t) = \Theta(N-v_pt)\,\psi^0(N-v_pt)\exp\{-\psi_1^0\int_0^t \mathrm{d}t'\, k(N-v_p[t-t'])\}$$

$$= \psi^0(0)\exp\left\{\frac{-\ln 2\int_0^N k}{\int_0^{\infty} k}\right\} \qquad (v_pt < N < n_0^* + v_pt) \quad \text{(B2)}$$

The last step follows after using the $N < n_0^*$ expression for ψ^0 from eq 23 and the result for ψ_1^0 of eq 21.

Consider first $t < \tau_{n_0^*}$. Then the MWD of eq B2 coincides with the steady state one from v_pt up to n_0^* and then has a very flat extended plateau portion in $n_0^* < N < n_0^* + v_pt$, where $\psi \approx (1/2)[1 + (z/N)^{1/2}]$. Turning now to larger N values, $N > n_0^* + v_pt$, such macroradicals always experience a field less than the field they would have experienced in steady state, namely H_s^0. Initially, this field is $H_s(t)$, which quickly drops well below H_s^0 (see eq 43). Suppose n_t^* "catches up" with this living chain at a certain time t^* when its length is N^*; its field then switches to $k(N^*)\psi_1^0$, and is thereafter equal to $k(N^*+v_p[t-t^*])\psi_1^0$, which is clearly less than $H_s^0 = k(n_0^*)\psi_1^0$. Thus ψ is approximately equal to the value it would have if its field were set to zero, $H = 0$ in eq 34:

$$\psi(N,t) \approx \psi^0(N-v_pt) \qquad (N > n_0^* + v_pt) \qquad \text{(B3)}$$

The larger N, the more accurate eq B3 becomes. In fact, it is shown in section IIIB that for $N \gg n_0^*$, the field is almost always much smaller than the steady state field. For these N eq B3 is very accurate; i.e., the MWD is the steady state one *translating* with speed v_p in the $+N$ direction. A rough depiction of the MWD for times

$\tau_{\mathrm{short}} < t < \tau_{n_0^*}$, as described by eqs B2 and B3, is shown in Figure 4b.

By the time $t = \tau_{n_0^*}$ the entire short chain population has disappeared (see Figure 4c). According to eq B3 this is exponential for $N \gtrsim 2n_0^*$, while for n_0^* it follows the extended plateau of eq B2. Since $n_0^* \ll \bar{N}$ (eq 14), we can absorb the plateau region into a single exponential with small error:

$$\frac{\psi(N,t)}{\psi^0(0)} \approx \Theta(N-n_0^*)\frac{1}{2}\mathrm{e}^{-(N-n_0^*)/\bar{N}} \qquad (t = \tau_{n_0^*}) \quad \text{(B4)}$$

Let us now show that for $t > \tau_{n_0^*}$ the distribution of Figure 4c, which is simply the steady state MWD with the short part ($N < n_0^*$) completely cut out, simply translates with speed v_{p} with almost no termination, since the short chains have disappeared. Consider the trailing edge of ψ at $N = v_{\mathrm{p}}t$, which experiences the largest field of any macroradical. Using eq B1, one finds the total termination probability for such macroradicals in the interval $\tau_{n_0^*} \rightarrow \tau_{\mathrm{rad}}$ is

$$P^{\mathrm{term}}(n_0^* \rightarrow \bar{N}, \tau_{n_0^*} \rightarrow \tau_{\mathrm{rad}}) \approx \frac{\psi_{\mathrm{l}}^0}{v_{\mathrm{p}}} \int_{n_0^*}^{\bar{N}} \mathrm{d}N\ k(N) \approx \left(\frac{z}{\bar{N}}\right)^{1/3} \ll 1 \quad \text{(B5)}$$

in which the integral is dominated by the lower limit. Typical living chains suffer a much smaller net termination probability than this. Thus, termination of the entire MWD is negligible and we have

$$\frac{\psi(N,t)}{\psi^0(0)} \approx \frac{1}{2}\mathrm{e}^{-(N-v_{\mathrm{p}}t)/\bar{N}} \qquad (\tau_{n_0^*} < t < \tau_{\mathrm{rad}}) \quad \text{(B6)}$$

This is shown in Figure 4d.

Appendix C. Posteffect at Intermediate Times, $\tau_{\mathrm{short}} < t < \tau_{\mathrm{rad}}$: Calculation of Long Chain Field $H_{\mathrm{s}}(t)$

In this appendix we estimate the long chain reaction field $H_{\mathrm{s}}(t)$ during posteffect for entangled FRPs, for times such that $z < v_{\mathrm{p}}t < \bar{N}$. We will often use the estimate $\int_N^\infty k \approx Nk(N)$ for $N > v_{\mathrm{p}}t$. Integrating by parts, we have

$$H_{\mathrm{s}}(t) = \int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\ k(M)\ \psi(M,t) = \psi(v_{\mathrm{p}}t,t) \int_{v_{\mathrm{p}}t}^{\infty} k + \int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\ \left(\int_M^\infty k\right)\ \psi'(M,t) \quad \text{(C1)}$$

where the prime in ψ' denotes differentiation with respect to M. The dominant contribution is the first term on the right hand side of eq C1. Consider now the correction term in eq C1. Substituting $\psi \approx (\psi^0(0)/2)[1 + (z/\bar{N})^{1/2}]$ for $v_{\mathrm{p}}t < N < n_0^* + v_{\mathrm{p}}t$ (obtained by expanding the exponent in the expression for ψ of eq B2), and substituting $\psi \approx (\psi^0(0)/2) \exp\{-(N - v_{\mathrm{p}}t)/\bar{N}\}$ for $N > n_0^* + v_{\mathrm{p}}t$ (see eq B3), one estimates this term as

$$\int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\ \left(\int_M^\infty k\right)\ \psi'(M,t) \approx \psi^0(0) \int_{v_{\mathrm{p}}t}^{n_0^*+v_{\mathrm{p}}t} \mathrm{d}M\ Mk(M)\frac{\mathrm{d}}{\mathrm{d}M}\left(\frac{z}{M}\right)^{1/2} + \psi^0(0)\int_{n_0^*+v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\ Mk(M)\frac{\mathrm{d}}{\mathrm{d}M} \exp\{-(M - v_{\mathrm{p}}t)/\bar{N}\} \quad \text{(C2)}$$

Now the first term on the right hand side of eq C2 is dominated by the lower limit $v_{\mathrm{p}}t$ and gives approximately $-\psi^0(0)\ k(z)\ z(\tau_{\mathrm{short}}/t)$. For $t \ll \tau_{\mathrm{rad}}$ the second term is approximately

$$\frac{-\psi^0(0)}{\bar{N}}\left[\int_0^\infty \mathrm{d}M\ k(M)M\mathrm{e}^{-M/\bar{N}} - \int_0^{n_0^*+v_{\mathrm{p}}t} \mathrm{d}M\ k(M)M\right] \quad \text{(C3)}$$

with errors of order (t/τ_{rad}). To within small corrections, we were able to replace $\exp\{-(M - v_{\mathrm{p}}t)/\bar{N}\}$ by $\exp\{-M/\bar{N}\}$ and to set the exponential in the second term to unity. Now the first term in the square brackets approximates $k(\bar{N})\bar{N}^2$, while in the second term the integral's upper limit dominates, giving approximately $k(n_0^* + v_{\mathrm{p}}t)(n_0^* + v_{\mathrm{p}}t)^2$, which gives a much smaller contribution since $\bar{N} \gg n_0^* + v_{\mathrm{p}}t$. Thus the relative magnitude of the correction term in eq C1 is

$$\frac{-\int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\left(\int_M^\infty k\right)\psi'}{\psi(v_{\mathrm{p}}t,t)\int_{v_{\mathrm{p}}t}^{\infty} k} \approx \frac{\psi^0(0)\ k(z)\ z\ (\tau_{\mathrm{short}}/t) + \psi^0(0)\ k(\bar{N})\bar{N}}{\psi^0(0)\ k(v_{\mathrm{p}}t)v_{\mathrm{p}}t} = \left(\frac{\tau_{\mathrm{short}}}{t}\right)^{1/2} + \left(\frac{t}{\tau_{\mathrm{rad}}}\right)^{1/2} \quad \text{(C4)}$$

and the reaction field reads

$$H_{\mathrm{s}}(t) = \int_{v_{\mathrm{p}}t}^{\infty} k\psi = \psi(v_{\mathrm{p}}t,t)\int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}N\ k(N)[1 + O(\tau_{\mathrm{short}}/t)^{1/2} + O(t/\tau_{\mathrm{rad}})^{1/2}] \qquad (\tau_{\mathrm{short}} < t < \tau_{\mathrm{rad}}) \quad \text{(C5)}$$

Appendix D. Posteffect at Long Times, $t \gg \tau_{\mathrm{rad}}$: Living MWD Approximately Monodisperse

In this appendix we calculate, for entangled FRPs at long times $t \gg \tau_{\mathrm{rad}}$, the total living chain termination rate, $R_{\mathrm{term}}^{\mathrm{total}}$, which during posteffect equals the rate of disappearance of living chains, $\mathrm{d}\psi_{\mathrm{l}}/\mathrm{d}t$:

$$R_{\mathrm{term}}^{\mathrm{total}} = \int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}N\ H(N,t)\ \psi(N,t), \qquad H(N,t) \equiv \int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\ k(M,N)\ \psi(N,t) \quad \text{(D1)}$$

In this limit we have $v_{\mathrm{p}}t \gg \bar{N}$, where $\bar{N}$ is the width of $\psi(N,t)$. Let us deal first with the reaction field H. Integrating by parts gives

$$H(N,t) = k(v_{\mathrm{p}}t,N)\int_{v_{\mathrm{p}}t}^{\infty} \psi + \int_{v_{\mathrm{p}}t}^{\infty} \mathrm{d}M\ \left(\int_M^\infty \psi\right)\frac{\mathrm{d}}{\mathrm{d}M}\ k(M,N) \quad \text{(D2)}$$

Now ψ is nonvanishing only for $N \geq v_{\mathrm{p}}t$ and then drops to zero sharply after its width of order $\bar{N}$. Meanwhile $k(M,N)$ can be written[36] as $k(\infty,N) \equiv k(N)$ multiplied by a crossover function $h(M/N)$ as in eq A2 of Appendix A. Thus

$$\psi(N,t) = \psi^0(0)\, q([N - v_\mathrm{p}t]/\bar{N}),\qquad k(M,N) = k(N)\, h(M/N) \quad \text{(D3)}$$

where $q(u<0) = 0$, both scaling functions $q(u)$ and $h(u)$ are of order unity for u of order unity, $q(u\gg 1) \rightarrow 0$ very rapidly, and $h(u\gg 1) = 1$.

Thus we can write $\int_M^\infty \psi = \psi^0(0)\bar{N}Q([M-v_\mathrm{p}t]/\bar{N})$ where $Q(u) \equiv \int_u^\infty q$ (and obeys $Q(0) \approx 1$, $Q(u\gg 1) \rightarrow 0$) and $\mathrm{d}k(M,N)/\mathrm{d}N = [k(N)\, h'(M/N)]/N$ where $h'(u) \equiv \mathrm{d}h(u)/\mathrm{d}u$. Equation D2 can now be rewritten

$$H(N,t) = k(v_\mathrm{p}t,N)\, \psi_\mathrm{l}(t) + \psi^0(0)\bar{N}\left[\frac{k(N)}{N}\right]\int_{v_\mathrm{p}t}^\infty \mathrm{d}M\, Q([M-v_\mathrm{p}t]/\bar{N})\, h'(M/N) \quad \text{(D4)}$$

We now show that the first term dominates H. Consider the integral in the second (correction) term above, in whose integrand the function Q constrains relevant M values to lie within order $\bar{N}$ of $v_\mathrm{p}t$. Hence one can replace $h'(M/N) \rightarrow h'(v_\mathrm{p}t/N)$ with small error. The remaining integral over M values then equals $\bar{N}\int_0^\infty \mathrm{d}u\ Q(u) \approx \bar{N}$. The entire correction term thus approximates $h'(v_\mathrm{p}t/N)\psi_\mathrm{l}^0 k(N)\bar{N}/N$, since $\psi^0(0)\bar{N} \approx \psi_\mathrm{l}^0$, providing a relative correction in eq D4 of magnitude

$$\frac{-[h'(v_\mathrm{p}t/N)/h(v_\mathrm{p}t/N)]\, k(v_\mathrm{p}t,N)\psi_l^0\bar{N}/N}{k(v_\mathrm{p}t,N)\psi_\mathrm{l}(t)} \approx \frac{\bar{N}}{N} \quad \text{(D5)}$$

after substituting $k(v_\mathrm{p}t,N) = k(N)\, h(v_\mathrm{p}t/N)$ and using $|h'(u)/h(u)| = O(1)$. Thus eq D4 gives

$$H(N,t) = k(v_\mathrm{p}t,N)\, \psi_\mathrm{l}(t)\{1 + O(\bar{N}/N)\} \quad \text{(D6)}$$

This completes the calculation of $H(N,t)$. Note that the correction term above is always small because the smallest living chains are of length $v_\mathrm{p}t$, which greatly exceeds $\bar{N}$ for these times.

Now let us calculate $R_\mathrm{term}^\mathrm{total}$ in eq D1, which after integration by parts gives

$$\begin{aligned} R_\mathrm{term}^\mathrm{total} &= H(v_\mathrm{p}t,t)\int_{v_\mathrm{p}t}^\infty \psi + \int_{v_\mathrm{p}t}^\infty \mathrm{d}M\, \left(\int_M^\infty \psi\right) \frac{\partial}{\partial M}H(M,t) \\ &\approx k(v_\mathrm{p}t,v_\mathrm{p}t)\psi_\mathrm{l}^{\,2}\{1 + O(\bar{N}/v_\mathrm{p}t)\} - \\ &\qquad \int_{v_\mathrm{p}t}^\infty \mathrm{d}M\, \psi^0(0)\bar{N}Q([M-v_\mathrm{p}t]/\bar{N}) \times \\ &\qquad k(v_\mathrm{p}t)(1/v_\mathrm{p}t)\, h'(M/v_\mathrm{p}t)\, \psi_\mathrm{l}(t) \quad \text{(D7)} \end{aligned}$$

We have used eq D3 for ψ and k and eq D6 for H. Proceeding similarly to our analysis of the correction term in eq D4, we replace $h'(M/v_\mathrm{p}t) \approx h'(1)$ and perform the M integral, which gives approximately $\psi_\mathrm{l}^2(t)[k(v_\mathrm{p}t)/v_\mathrm{p}t]\bar{N}$ for the second term on the right hand side of eq D7 after using $\psi_\mathrm{l}(t) \approx \psi_\mathrm{l}^0$. This is a correction term of order $\bar{N}/v_\mathrm{p}t$ relative to $k(v_\mathrm{p}t,v_\mathrm{p}t)\psi_\mathrm{l}^2$. Thus

$$R_\mathrm{term}^\mathrm{total} = k(v_\mathrm{p}t,v_\mathrm{p}t)\, \psi_\mathrm{l}^{\,2}(t)\{1 + O(\bar{N}/v_\mathrm{p}t)\} \qquad (v_\mathrm{p}t \gg \bar{N}) \quad \text{(D8)}$$

which leads to eq 46 in the main text.

References and Notes

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(25) Termination by reaction of two living chains may also result in two dead chains, not one. The relative frequency of such so-called disproportionation events, which are due to hydrogen abstraction, depends on the polymerizing material. This is irrelevant for our purposes; all that matters is that each termination event annihilates two living chains.

(26) We adopt the standard approximation that the dead chain solution is a fixed environment for the living dynamics. As is well-known, the dead chain solution changes quasi-statically over a much longer time scale than characteristic living population time scales.

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MA971616K