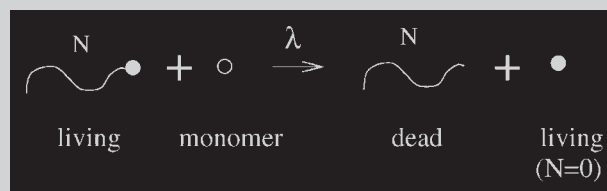


Full Paper: Pulsed laser polymerization (PLP) is widely employed to measure propagation rate coefficients k_p in free radical polymerization. Various properties of PLP have been established in previous works, mainly using numerical methods. The objective of this paper is to obtain analytical results. We obtain the most general analytical solution for the dead chain molecular weight distribution (MWD) under low conversion conditions which has been hitherto obtained. Simultaneous disproportionation and combination termination processes are treated. The hallmarks of PLP are the dead MWD discontinuities located at integer multiples of $n_0 = k_p t_0 C_M$, where t_0 is the laser period and C_M is the monomer concentration. We show that chain transfer reduces their amplitude by factors $e^{-c_{tr} L n_0}$, consistent with numerical results obtained by other workers. Here c_{tr} is the chain transfer coefficient and $L n_0$ ($L = \text{integer}$) are the discontinuity locations. Additionally, transfer generates a small amplitude continuous contribution to the MWD. These results generalize earlier analytical results which were obtained for the case of disproportionation only. We also considered two classes of broadening: (i) Poisson broadening of growing living chains

and (ii) intrinsic broadening by the MWD measuring equipment (typically gel permeation chromatography, GPC). Broadening smoothes the MWD discontinuities. Under typical PLP experimental conditions, the associated inflection points are very close to the discontinuities of the unbroadened MWD. Previous numerical works have indicated that the optimal procedure is to use the inflection point to infer k_p . We prove that this is a correct procedure provided the GPC resolution σ is better than $n_0^{1/2}$. Otherwise this underestimates $L n_0$ by an amount of order σ^2/n_0 .



Schematic of a chain transfer reaction with monomer as the transfer agent.

Pulsed Laser Polymerization at Low Conversions: Broadening and Chain Transfer Effects

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Received: January 14, 2003; Revised: April 16, 2003; Accepted: April 28, 2003; DOI: 10.1002/mats.200350001

Keywords: molecular weight distribution/molar mass distribution; propagation rate coefficients; pulsed laser polymerization; radical polymerization; theory

Introduction

A fundamental material parameter in free radical polymerization (FRP) is the propagation rate constant^[1–3] k_p governing the sequential addition of monomers to the active free-radical ends of “living” chains (see Figure 1). In this paper we consider theoretically “pulsed laser polymerization” (PLP),^[4,5] possibly the most accurate method to measure k_p . In PLP new radicals (living chains of one monomer, $N=1$) are generated by a sequence of laser pulses which photocleave photoinitiators in the reaction mix. The laser is flashed periodically (the duration of each flash is extremely short (see Figure 5(a))) with flash period $t_0 \sim 0.1$ s optimally chosen to be somewhat shorter than the average living chain lifetime. Thus every t_0 the living chain population is updated by the injection of new primary radicals. After many cycles a periodic state is established

where the time averaged rate of radical production balances the time averaged rate of living chain termination: pairs of living chains terminate to generate either a single (“combination”) or a pair (“disproportionation”) of “dead” chains, the final polymer product (see Figure 2).

Now unlike the dead molecular weight distribution (MWD) of standard steady state FRP which has no singular features, in the case of PLP the dead MWD, $\phi_{dead}(N)$, is predicted theoretically to possess finite discontinuities^[3,6] at chain lengths $N = L n_0$, where $L = 0, 1, 2, \dots$ and

$$n_0 \equiv v_p t_0, \quad v_p \equiv k_p C_M \quad (1)$$

Here n_0 is the number of monomers added to a growing living chain in time t_0 and the “propagation velocity” v_p , namely the rate of monomer addition to a growing chain, is proportional to the monomer concentration C_M . The origin

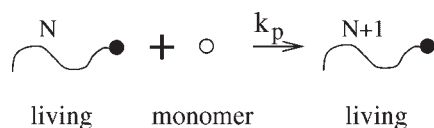


Figure 1. Schematic of monomer addition to the free radical end of a living chain.

of the dead MWD discontinuities is the coherent sudden increase in termination rates due to the sudden increase in radical population following each pulse. In principle the discontinuities can be seen experimentally after measuring the resulting MWD by gel permeation chromatography (GPC). Thus n_0 and hence v_p (or equivalently k_p) is inferred. This method has been employed to deduce k_p for a variety of polymerizing systems.^[7-12]

In reality there exist a number of practical difficulties. (1) Broadening effects. Consider a living chain created at $t = 0$. After time t_0 its length is not exactly $v_p t_0$; since polymerization is a random process, Poisson fluctuations arise around this length. This then leads to a softening of the theoretically infinitely sharp dead MWD discontinuities. Another, but quite different effect is the direct broadening of the dead MWD due to intrinsic uncertainties in the measuring method. GPC equipment if supplied with a discontinuous dead MWD will output a reading indicative of a somewhat broadened discontinuity due to fluctuations in the transit time of a chain of a given length through the gel. (2) Chain transfer^[1] of radicals from living chain ends to surrounding unpolymerized monomer (Figure 3), quantified by the parameter λ . This is simply related to the chain transfer coefficient c_{tr} :

$$c_{tr} \equiv \frac{k_{tr} C_X}{k_p C_M} = \frac{\lambda}{v_p} \quad (2)$$

where k_{tr} is the 2nd order rate constant governing chain transfer to species X whose concentration is C_X (X is usually the monomer species). One expects chain transfer, important for species such as vinyl acetate and

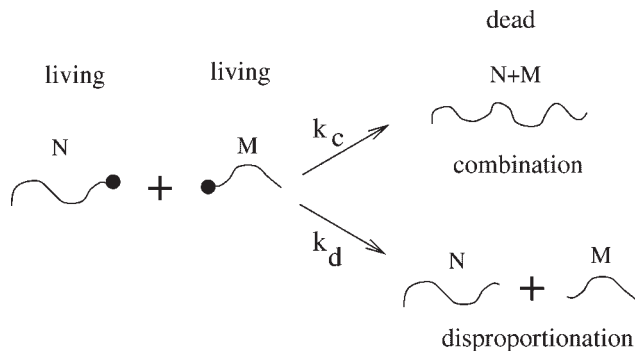


Figure 2. Termination reaction of two living chains of length N and M . Combination results into one dead chain of length $N + M$ while disproportionation results into two dead chains of length N and M .

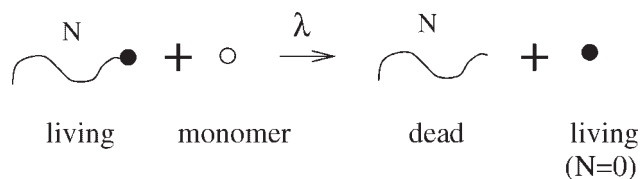


Figure 3. Schematic of a chain transfer reaction with monomer as the transfer agent.

polystyrene,^[11,13] to dephase the living MWD which would otherwise be a sequence of in-phase pulses. This will then affect the discontinuities in the dead MWD.

Typical experimental MWDs produced by PLP are shown in Figure 4 where an obviously broadened first discontinuity is evident near molecular weight 40,000. In order to deduce the correct propagation rate constant, it is essential to have an algorithm to infer n_0 from such a broadened discontinuity. Taking n_0 as the molecular weight corresponding to the lower point of inflection, near the middle of the broadened discontinuity, has been proposed as the optimal approach.^[6,14] Other authors have advocated that under particular conditions this criterion should be replaced with the maximum point.^[15,16]

In order to design and interpret PLP experiments many researchers have employed numerical simulations of PLP chemical kinetics. By varying the parameters of the simulations the resulting dead MWD is modeled under different experimental conditions. In such numerical studies Poisson-broadening is automatically taken into account and numerous side-reactions such as chain transfer can be incorporated. Guidelines can then be derived for extracting k_p from the broadened MWD peak. Such numerical approaches have so far been employed both in the

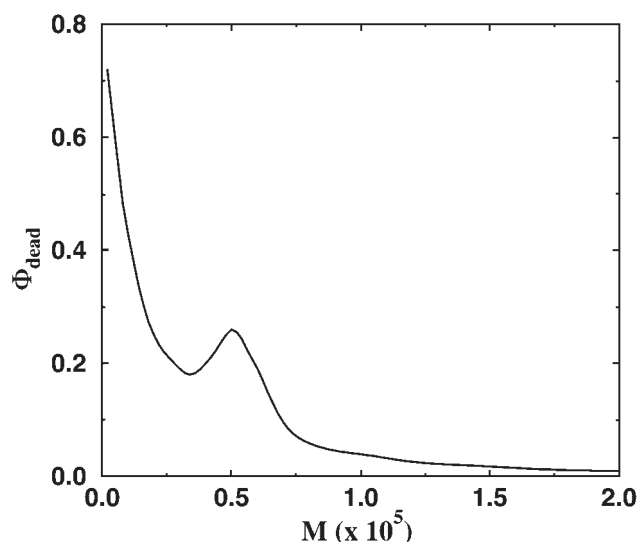


Figure 4. MWD of poly(methyl methacrylate) produced at 40°C by PLP with $t_0 = 0.1$ s as measured in ref.^[7] Horizontal axis is molecular weight. Arbitrary units on vertical axis.

absence^[11,17,18] and the presence of chain transfer.^[13,16,19] The effects of experimental broadening have been addressed numerically in ref.^[16,17]

Analytical solutions of PLP dynamics are also very desirable. Where available they provide a systematic and quantitative framework which exactly articulates the conclusions of the underlying physical model, beyond the scope of numerical analyses. Analytical expressions can also greatly facilitate experimental design by obviating the need for numerical work. The first analytical solution of PLP dynamics appeared in ref.^[6,20] and included the effects of Poisson broadening for termination by both combination and disproportionation. A new derivation and a review of these theoretical results is given in ref.^[21] A closed form for the dead MWD for arbitrary sequences of laser pulses was derived in ref.^[22] Analytical work including chain transfer exists for the case of termination by disproportionation only.^[23,24]

In this paper we develop a completely general analytical theory for PLP, including the effects of broadening and chain transfer analytically. We thus quantify the effect of these two mechanisms on the theoretically infinitely sharp dead MWD which enables us to discuss the validity of empirical rules on deriving k_p from the broadened MWD peak. We consider a general (and typical) situation where both combination and disproportionation events occur. This extends previous analytical studies. We derive the most general analytical expressions which have been obtained hitherto for PLP, to the best of our knowledge. Closed expressions are derived in terms of the following independent parameters: ν_p , k_c , k_d , λ , t_0 , and the concentration of radicals produced per laser pulse. Here k_c and k_d are the combination and disproportionation rate constants, respectively (see Figure 2). An important quantity in what follows is the *net* termination rate constant,

$$k \equiv k_c + k_d \quad (3)$$

Our analysis describes low conversion FRP which allows us to make the approximation that the net living-living bimolecular termination rate constant, k , is independent of chain length (see Figure 2). In reality $k(M,N)$ depends on the degrees of polymerization M,N of the reacting chains. However in dilute solutions (under good solvent conditions) theory^[25–27] predicts a very weak dependence on chain lengths: $k(N,N) \sim N^{-\alpha}$ with $\alpha \approx 0.16$. A very weak dependence of k on chain lengths has also been well established experimentally in phosphorescence quenching studies.^[28] At low conversions, living chain terminations occur in a pure monomer solvent (usually a good one) and thus the approximation of constant k is expected to yield rather accurate conclusions. Making this approximation, all quantities can be calculated exactly. The effect of the dependence of termination rates on chain length has been addressed numerically in ref.^[18,29–34] which employed various empirical rules for the form of $k(M,N)$.

The living MWD, $\phi(N,t)$, like all quantities settles down to a periodic form with period t_0 . Bimolecular reactions as in Figure 2, 3 generate dead chains of length N at a rate

$$\dot{\phi}_{dead}(N,t) = \frac{1}{2}k_c \int_0^N dM \phi(M,t) \phi(N-M,t) + k_d \phi(N,t) \Psi(t) + \lambda \phi(N,t) \quad (4)$$

where Ψ is the total concentration of living chains. The resulting dead MWD will include Poisson broadening effects provided one uses the correct Poisson broadened living MWD in Equation (4). In the following we will employ the notation ϕ_{dead} to denote the dead MWD without Poisson broadening, including however chain transfer effects (i.e. ϕ_{dead} results from using in Equation (4) the form for $\phi(N,t)$ which correctly includes chain transfer but which neglects Poisson broadening). The full Poisson broadened MWD is denoted ϕ_{dead}^{broad} while the reading output by the GPC measuring equipment we name ϕ_{dead}^{read} .

The dead MWD is calculated in successive steps as follows. In the following section we review “ideal” PLP, i.e. we ignore chain transfer (setting $\lambda = 0$) and broadening effects. The time averaged dead MWD, ϕ_{dead}^{ideal} , turns out to have finite discontinuities at $N = jn_0$ (j is a positive integer). In the section on “Chain Transfer” we generalize the results of section on “Ideal PLP” to include chain transfer and express the resulting dead MWD, ϕ_{dead} , in terms of ϕ_{dead}^{ideal} . We find that chain transfer diminishes the amplitude of the dead MWD discontinuities, but does not broaden them. Broadening effects due to both Poisson broadening and due to limited experimental resolution are included in section on “Broadening and the Inflection Point Rule”. We show that the inflection point rule is correct for inferring n_0 only when the width of the Poisson broadened discontinuity is larger than the experimental resolution. We conclude with a summary of our results.

Throughout, $[N]$ will denote the nearest integer to N/n_0 which is less than N/n_0 , whilst $rN = \text{rem}[N, n_0]$ denotes the remainder of N modulo n_0 . Similar notation will apply to time t , with n_0 replaced by t_0 . Thus

$$\begin{aligned} N &\equiv [N]n_0 + rN, & rN &\equiv \text{rem}[N, n_0]; \\ t &\equiv [t]t_0 + rt, & rt &\equiv \text{rem}[t, t_0] \end{aligned} \quad (5)$$

Ideal PLP

Let us first briefly review the “ideal” PLP problem ignoring the effects of broadening and chain transfer, as analyzed by Olaj et al.^[6,21] Termination may occur either by combination or disproportionation reactions. First we calculate the living MWD which depends on the total termination rate constant, k , only, and not on the mode of termination. We then derive separate expressions for the dead chains terminated by combination and disproportionation, respectively.

Total Concentration of Living Chains $\Psi(t)$ and Reaction Field $H(t)$

The number density MWD of living chains, $\phi(N,t)$, obeys

$$\dot{\phi} = -v_p\phi' - H(t)\phi + \delta(N)R_i(t) \quad (6)$$

with $\phi(N < 0, t) = 0$. Here $\dot{\phi} \equiv \partial\phi/\partial t$ and $\phi' \equiv \partial\phi/\partial N$. Note that the $\delta(N)R_i(t)$ term which injects primary radicals (chains of length $N=0$ in our continuous framework) into the system at rate $R_i(t)$ per unit volume, is equivalent to the boundary condition $v_p\phi(0,t) = R_i(t)$. In PLP dynamics the time-dependent primary radical production rate, $R_i(t)$, is a train of pulses,

$$R_i(t) = \bar{R}_i t_0 \sum_{j=-\infty}^{\infty} \delta(t + jt_0) \quad (7)$$

as shown in Figure 5(a). \bar{R}_i is the time averaged radical production rate. The $-v_p\phi'$ term in Equation (6) describes propagation whilst $H(t)\phi(N,t)$ is the total termination rate (due to both combination and disproportionation) for a chain of length N due to the "reaction field" $H(t)$, namely the total termination rate per unit time for a given chain due to all other chains in the system:

$$H(t) \equiv k\Psi(t), \quad \Psi(t) \equiv \int_0^{\infty} dN\phi(N,t) \quad (8)$$

Here $\Psi(t)$ is the total number density of living chains whose dynamics follow after integrating Equation (6) over all positive N values:

$$\dot{\Psi} = -H(t)\Psi + R_i(t) = -k\Psi^2 + R_i(t) \quad (9)$$

For t different from integer multiples of t_0 one has $R_i(t) = 0$ and thus Ψ obeys simple second order reaction kinetics, $\dot{\Psi} = -k\Psi^2$, with solution

$$\Psi(t) = \frac{\Psi_0}{1 + tk\Psi_0} \quad (0 < t < t_0) \quad (10)$$

where $\Psi_0 \equiv \Psi(0^+)$ is the value of Ψ just after a new laser pulse at $t=0$. We define β as the surviving fraction just before the next pulse at t_0 ,

$$\beta \equiv \Psi(t_0^-)/\Psi_0 \quad (11)$$

The values of Ψ_0 and β when the system settles down to a periodic stationary state are determined in terms of \bar{R}_i , k , and t_0 , by equating the number of terminated chains in one cycle with the number of new living chains introduced by a pulse,

$$(1 - \beta)\Psi_0 = \bar{R}_i t_0 \quad (12)$$

This relation together with Equation (10) and (11) yields

$$\Psi_0 = \frac{1}{2} \bar{R}_i t_0 [1 + \{1 + 4/(\bar{R}_i k t_0^2)\}^{1/2}],$$

$$\beta = \frac{1}{1 + k\Psi_0 t_0} \quad (13)$$

The steady state $\Psi(t)$, sketched in Figure 5(c), is of course

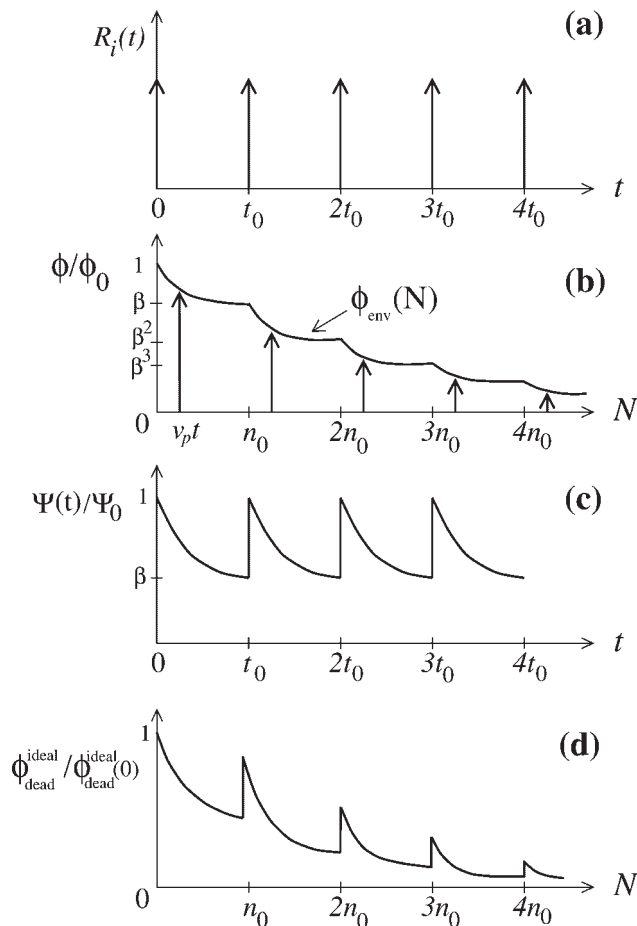


Figure 5. (a) Rate of radical production as a function of time. $R_i(t)$ is non-zero only during the short duration of the laser pulse the period of which is t_0 . (b) Snapshot of the living chain MWD $\phi(N,t)$ during $0 < t < t_0$ in the ideal case (absence of chain transfer and Poisson broadening). Here $\phi_0 \equiv \phi(0)$. ϕ consists of a series of δ -function pulses whose amplitude follows the envelope $\phi_{env}(N)$. (c) Number density of living chains as a function of time (see Equation (10)). (d) Dead MWD in the ideal case. ϕ_{dead}^{ideal} is discontinuous at integer multiples of n_0 .

periodic with period t_0 , and has discontinuous jumps $\Delta\Psi = (1 - \beta)\Psi_0$ at integer multiples of t_0 .

Living MWD

The solution to Equation (6) is derived in appendix A for a general $R_i(t)$ in terms of $H(t)$ whose important properties are derived in Appendix B. Using the present periodic form for $R_i(t)$, Equation (7), using Equation (12) and (B2) and recalling the periodicity of Ψ and H , we have

$$\phi(N,t) = (1 - \beta)\Psi_0 \Theta(N) \sum_{j=-\infty}^{\infty} e^{-\int_0^{N/v_p} H(t') dt'} \times \delta(N - v_p t - j n_0) = \sum_{j=-\infty}^{\infty} \phi_{env}(N) \delta(N - v_p t - j n_0) \quad (14)$$

where Θ is the step function ($\Theta(x > 0) = 1$, $\Theta(x < 0) = 0$) and the function ϕ_{env} , sketched in Figure 5(b), is the living MWD envelope

$$\begin{aligned}\phi_{env}(N) &\equiv \Theta(N)\beta^{[N]}(1-\beta)\Psi(N/v_p) \\ &= \Theta(N)\beta^{[N]}(1-\beta)\frac{\Psi_0}{1+k\Psi_0rN/v_p}\end{aligned}\quad (15)$$

The living MWD, sketched in Figure 5(b), is a train of pulses in phase with $R_i(t)$. A new δ -pulse is born at $N=0$ at time $t=0$, say, and then moves in the $+N$ direction with velocity v_p . When in the interval $(j-1)n_0 < N \leq jn_0$ (the “ j th sector”) this pulse suffers the same field $H(t)$ as in all other sectors. The amplitude of the δ -pulse in sector $j+1$ is thus reduced by a factor β with respect to sector j and follows the envelope $\phi_{env}(N)$.

Dead MWD

The time-averaged rate of dead chain generation, $\bar{\phi}_{dead}^{ideal}(N)$, is the sum of the contributions due to termination by combination and disproportionation, $\bar{\phi}_{dead}^{ideal}(N) = \bar{\phi}_{dead}^{comb}(N) + \bar{\phi}_{dead}^{disp}(N)$. Each of these two contributions can be found by inserting Equation (14) into the first and second terms on the rhs of Equation (4), respectively, and then time averaging over one period. In the following we will use however a simpler method.

Consider first chains terminated by combination. We notice that, due to periodicity, the total concentration of dead chains of length N produced by combination per period, $\bar{\phi}_{dead}^{comb}(N)t_0$, equals one half the concentration of dead chains produced by combination by one single δ pulse throughout its entire lifetime. Thus choosing the $j=0$ pulse in Equation (14), bimolecular kinetics imply

$$\begin{aligned}\bar{\phi}_{dead}^{comb}(N) &= \frac{k_c}{2t_0} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dM \phi_{env}(M) \\ &\quad \times \delta(M - v_p t) \phi(N - M, t)\end{aligned}\quad (16)$$

This is proved rigorously in Appendix C. Since the integrand of Equation (16) is zero for negative t and M values, we have extended the lower limits of the integrals from 0 to $-\infty$ for future convenience.

Substituting the expression for ϕ of Equation (14) into the above expression, it is shown in Appendix D this leads to

$$\bar{\phi}_{dead}^{comb}(N) = C \frac{k_c}{k} \left\{ (L+1)\beta^L f^2 \left(\frac{rN}{2} \right) + L\beta^{L-1} f^2 \left(\frac{rN+n_0}{2} \right) \right\}\quad (17)$$

where

$$\begin{aligned}N &\equiv Ln_0 + rN, & f(n) &\equiv \frac{\beta}{\beta + (1-\beta)n/n_0}, \\ C &\equiv \frac{k\Psi_0^2(1-\beta)^2}{4v_p t_0}\end{aligned}\quad (18)$$

Similarly, the time-averaged concentration of dead chains generated by disproportionation can be calculated by noting that $\bar{\phi}_{dead}^{disp}(N)t_0$ is equal to the concentration of dead chains of length N produced by disproportionation by one single δ -pulse throughout its lifetime. Choosing $j=0$ for this pulse in Equation (14) one has

$$\bar{\phi}_{dead}^{disp}(N) = \frac{k_d}{t_0} \int_{-\infty}^{\infty} dt \phi_{env}(N) \delta(N - v_p t) \Psi(t)\quad (19)$$

Integrating the δ function in Equation (19) and using Equation (15) to express ϕ_{env} in terms of Ψ yields

$$\bar{\phi}_{dead}^{disp}(N) = 4C \frac{k_d}{k} \left\{ \frac{\beta^L}{1-\beta} f^2(rN) \right\}, \quad N \equiv Ln_0 + rN\quad (20)$$

The dead MWD, $\phi_{dead}^{ideal} = t\bar{\phi}_{dead}^{ideal} = t(\bar{\phi}_{dead}^{comb} + \bar{\phi}_{dead}^{disp})$, is shown in Figure 5(d). Both combination and disproportionation contributions have discontinuities at the end of each sector L (where $L=0$ labels the first sector, $0 \leq N \leq n_0$). The discontinuity, $\Delta\phi_{dead}^{ideal}$, at the boundary of sectors $L-1$ and L is

$$\begin{aligned}\frac{\Delta\phi_{dead}^{ideal}(Ln_0)}{\phi_{dead}^{ideal}(0)} &\equiv \frac{\phi_{dead}^{ideal}(Ln_0^+) - \phi_{dead}^{ideal}(Ln_0^-)}{\phi_{dead}^{ideal}(0)} \\ &= \beta^L \frac{2 + 4\rho}{1 + 4\rho/(1-\beta)}, \quad \rho \equiv k_d/k_c\end{aligned}\quad (21)$$

Chain Transfer

In this section we will study how chain transfer modifies the results of the preceding section. Each transfer event results in one dead chain of length N and one living chain of length $N=0$ as depicted in Figure 3.

Living MWD

The living dynamics now include additional loss through transfer from chains of length N . These radicals are reinjected as a source term at $N=0$:

$$\dot{\phi} = -v_p \phi' - [H(t) + \lambda]\phi + [R_i(t) + \lambda\Psi(t)]\delta(N)\quad (22)$$

The total reinjection rate is $\lambda\Psi$ where λ is defined in terms of the chain transfer coefficient in Equation (2).

Integrating Equation (22) over all positive N values (ϕ is zero for negative N) one immediately sees that the total number density of living chains $\Psi(t)$ obeys the same dynamics as without chain transfer, Equation (9). This must be true, of course, since transfer events conserve the total number of living chains and k is independent of chain length in the present approximation. The crucial point is that $\Psi(t)$ and $H(t) = -k\Psi(t)$ appearing in Equation (22) are the same periodic functions of time as without chain transfer, Equation (10).

Since $H(t)$ is a known function of time, the dynamics of Equation (22) are effectively linear and we can use the superposition principle to write $\phi = \phi_{coh} + \phi_{inc}$ where

$$\begin{aligned}\dot{\phi}_{coh} &= -v_p \phi'_{coh} - [H(t) + \lambda] \phi_{coh} + R_i(t) \delta(N) \\ \dot{\phi}_{inc} &= -v_p \phi'_{inc} - [H(t) + \lambda] \phi_{inc} + \lambda \Psi(t) \delta(N)\end{aligned}\quad (23)$$

Here ϕ_{coh} is the coherent part, which as we will immediately see is a sum of pulses in phase with radical production, whilst ϕ_{inc} is the incoherent part which is out of phase due to random transfer events.

Replacing $H \rightarrow H + \lambda$ in the general solution, Equation (A3), to the living dynamics without chain transfer, one sees ϕ_{coh} is $e^{-\lambda N/v_p}$ times its no-transfer form of Equation (14). Similarly replacing $H \rightarrow H + \lambda$ and $R_i \rightarrow \lambda \Psi$, one obtains ϕ_{inc} after using Equation (B2). One finds:

$$\begin{aligned}\phi_{coh}(N, t) &= e^{-\lambda N/v_p} \sum_{j=-\infty}^{\infty} \phi_{env}(N) \delta(N - v_p t - j n_0), \\ \Psi_{coh}(t) &= \Psi(t) \frac{(1 - \beta) e^{-\lambda t}}{1 - \beta e^{-\lambda t_0}} \\ \phi_{inc}(N, t) &= \frac{\lambda e^{-\lambda N/v_p}}{v_p} \Psi(t) \beta^{[t] - [t - N/v_p]} \Theta(N), \\ \Psi_{inc}(t) &= \Psi(t) - \Psi_{coh}(t)\end{aligned}\quad (24)$$

where Ψ_{coh} , Ψ_{inc} are the corresponding total concentrations of chains in each part of the MWD. ϕ_{inc} is a series of propagating pulses each of width n_0 , the amplitude of which decreases with molecular weight and time. Notice however that unlike ϕ_{coh} , ϕ_{inc} extends over all N values at a given time. ϕ_{inc} has discontinuities at $N = v_p t + j n_0$. At each discontinuity, ϕ_{inc} decreases suddenly by a factor β .

Dead MWD

Dead chains are generated by both living chain termination (first two terms on the rhs of Equation (4)) and chain transfer events (last term of Equation (4)). We consider first the contribution due to termination by combination. Using the results of Appendix C, the time averaged rate of production of dead chains by combination is given by

$$\begin{aligned}\bar{\phi}_{dead}^{comb}(N) &= \frac{k_c}{2t_0} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dM e^{-\lambda M/v_p} \phi_{env}(M) \delta(M - v_p t) \\ &\quad \times \{ \phi_{coh}(N - M, t) + 2\phi_{inc}(N - M, t) \}\end{aligned}\quad (25)$$

This is the contribution to $\bar{\phi}_{dead}$ due to termination by combination by one single δ pulse belonging to the coherent living MWD, throughout its lifetime. Combination occurs either with other coherent chains or by ‘‘cross-coupling’’ with chains belonging to ϕ_{inc} . In Equation (25) we have assumed that chain transfer is a weak effect, i.e. that λ is

small in a sense to be quantified below, and we keep the leading correction only. Thus we discarded the $O(\lambda^2)$ $\phi_{inc} \phi_{inc}$ termination term.

Now the coherent-coherent coupling term in Equation (25) is equal to that of Equation (16), multiplied by $e^{-\lambda N/v_p}$. The only difficulty is the coherent-incoherent cross-term $\bar{\phi}_{dead, cross}^{comb}$. In Appendix E it is shown that

$$\begin{aligned}\bar{\phi}_{dead, cross}^{comb}(N) &= \frac{\lambda e^{-\lambda N/v_p} k_c}{v_p t_0} \frac{1}{k} (1 - \beta) \left\{ \beta^L [(L + 1)\beta - L] \Psi_0 \right. \\ &\quad \left. + \beta^L (L + 1)(1 - \beta) \Psi \left(\frac{rN}{2v_p} \right) + L\beta^{L-1} (1 - \beta) \right. \\ &\quad \left. \times \Psi \left(\frac{rN + n_0}{2v_p} \right) - \beta^L \Psi \left(\frac{rN}{v_p} \right) \right\}\end{aligned}\quad (26)$$

Let us calculate now the disproportionation and chain transfer contributions, $\bar{\phi}_{dead}^{disp}$ and $\bar{\phi}_{dead}^{trans}$. Time averaging the last two terms of Equation (4) one has (bar denotes time average)

$$\bar{\phi}_{dead}^{disp}(N) + \bar{\phi}_{dead}^{trans}(N) = k_d \bar{\phi(N)} \bar{\Psi} + \lambda \bar{\phi}(N)\quad (27)$$

Now from Equation (22) one has $k \bar{\phi(N)} \bar{\Psi} + \lambda \bar{\phi}(N) = -v_p \partial \bar{\phi} / \partial N$, using $\bar{\phi} = 0$ in stationary state. Thus using Equation (27),

$$\bar{\phi}_{dead}^{disp}(N) + \bar{\phi}_{dead}^{trans}(N) = -\frac{k_d}{k} v_p \frac{\partial \bar{\phi}}{\partial N} + \frac{k_c}{k} \lambda \bar{\phi}(N)\quad (28)$$

The rhs of Equation (28) is calculated in Appendix F (see Equation (F5)) using the expressions for ϕ derived in the section on ‘‘Living MWD’’.

Thus collecting all terms, $\bar{\phi}_{dead} = \bar{\phi}_{dead}^{comb} + \bar{\phi}_{dead}^{disp} + \bar{\phi}_{dead}^{trans}$, and noticing that the k_d/k term of Equation (F5) cancels the last term of Equation (26), we have

$$\begin{aligned}\bar{\phi}_{dead}(N) &= e^{-\lambda N/v_p} \left\{ \bar{\phi}_{dead}^{ideal}(N) + \varepsilon \bar{\phi}_{dead}^{inc}(N) \right\}, \\ \varepsilon &\equiv \frac{4\lambda}{(1 - \beta)k\Psi_0} = \frac{4\lambda\beta t_0}{(1 - \beta)^2}\end{aligned}\quad (29)$$

where

$$\begin{aligned}\bar{\phi}_{dead}^{inc}(N) &\equiv C \left[\frac{k_c}{k} \left\{ \beta^L [(L + 1)\beta - L] + \beta^L (L + 1)(1 - \beta) \right. \right. \\ &\quad \left. \left. \times f \left(\frac{rN}{2} \right) + L\beta^{L-1} (1 - \beta) f \left(\frac{rN + n_0}{2} \right) \right\} \right. \\ &\quad \left. + 2 \frac{k_d}{k} \beta^L f(rN) \right]\end{aligned}\quad (30)$$

The two contributions to the dead MWD, $\phi_{dead} = t \bar{\phi}_{dead}$, are plotted in Figure 6. The incoherent part due to transfer events has no discontinuities, i.e. $\bar{\phi}_{dead}^{inc}(Ln_0^-) = \bar{\phi}_{dead}^{inc}(Ln_0^+)$, as may be seen using Equation (18). It is proportional to the small parameter $\varepsilon \approx \lambda t_0$.

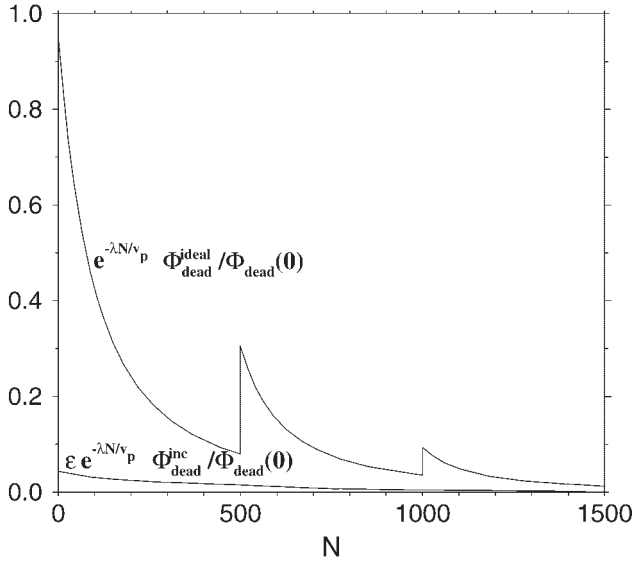


Figure 6. Contributions to the dead MWD in the presence of chain transfer. The upper curve is the *coherent* contribution. The lower curve is the *incoherent* contribution, proportional to the small parameter ϵ . The slope of the incoherent MWD is discontinuous at integer multiples of n_0 . Values of parameters used: $v_p = 5000 \text{ s}^{-1}$, $k_c = k_d = 2 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $\lambda = 0.5 \text{ s}^{-1}$, $t_0 = .1 \text{ s}$, $R_{i0} = 5 \cdot 10^{-7} \text{ M}$.

Since the only discontinuous term in Equation (29) is $\bar{\phi}_{dead}^{ideal}$, using Equation (21) the discontinuity at $N = Ln_0$ is

$$\frac{\Delta \phi_{dead}(Ln_0)}{\phi_{dead}(0)} = e^{-\lambda Ln_0} \beta^L \frac{2 + 4\rho}{1 + 4\rho/(1 - \beta) + \epsilon(1 + 2\rho)} \quad (31)$$

where $\Delta \phi_{dead}(Ln_0) \equiv \phi_{dead}(Ln_0^+) - \phi_{dead}(Ln_0^-)$.

Broadening and the Inflection Point Rule

The MWD derived in the previous section, Equation (29), has ignored (i) Poisson broadening and (ii) broadening due to the limited accuracy of GPC measurements.

Consider first Poisson broadening. The true length distribution of a chain growing with mean velocity v_p is not $\delta(N - v_p t)$ as has been assumed above, but rather the Poisson distribution (see Figure 7) which for large N tends to a Gaussian:

$$P_t(N) = \frac{(v_p t)^N}{N!} e^{-v_p t} \approx c e^{-(N - v_p t)^2 / (2v_p t)}, \quad (N \gg 1) \quad (32)$$

Here $c = (2\pi v_p t)^{-1/2}$ is a normalization constant.

Now since the termination rate constant k is independent of chain length, clearly broadening leaves the total number of living chains $\Psi(t)$ unchanged. Hence the field $H(t)$ is unchanged, and thus a group of living chains injected at $t=0$ are still depleted in number by the factor $e^{-\int_0^t H}$ after time t , regardless of which chains are a little longer than $v_p t$ and which a little shorter.

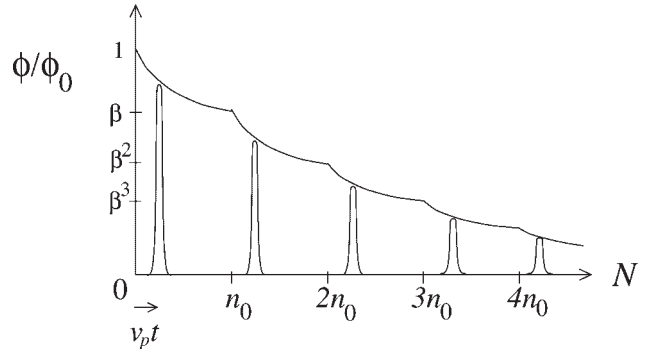


Figure 7. Snapshot of living MWD including the effects of Poisson broadening: the δ -functions of the living MWD of Figure 5(b) are replaced by Gaussians.

Moreover we show in Appendix G that even in the presence of chain transfer, the Poisson broadened living MWD, $\phi_{broad}(N)$, can be expressed in terms of the unbroadened living MWD, $\phi(N)$, calculated in the previous sections as follows:

$$\phi_{broad}(N, t) = \int_{-\infty}^{\infty} dM \phi(M, t) \Delta(N; M),$$

$$\Delta(N; \bar{N}) \equiv \frac{1}{\sqrt{2\pi\bar{N}}} e^{-(N - \bar{N})^2 / (2\bar{N})} \quad (33)$$

Thus the δ -pulses of ϕ in Equation (14) (or of ϕ_{coh} in Equation (24) if chain transfer is present) are replaced by Δ 's, namely Gaussians of mean \bar{N} and width $\sqrt{\bar{N}}$. Note that with increasing \bar{N} , the relative width of the broadened Δ -functions decreases as $1/\sqrt{\bar{N}}$.

Then substituting Equation (33) into Equation (4) we find that the dead MWD, ϕ_{dead}^{broad} , is also obtained by integrating the dead MWD in the absence of Poisson broadening, Equation (29), against a Δ function:

$$\phi_{dead}^{broad}(N) = \int_{-\infty}^{\infty} dM \phi_{dead}(M) \Delta(N; M) \quad (34)$$

(We used the identity $\int_{-\infty}^{\infty} dM \Delta(M; P) \Delta(N - M; L) = \Delta(N; L + P)$ for the termination by combination term of Equation (4)). Here $\phi_{dead} = t \phi_{dead}$. An example of the broadened MWD is shown in Figure 8, where ϕ_{dead}^{broad} is calculated by numerical integration of Equation (34). Equation (34) has been called “a posteriori Poisson broadening”.^[21] In the present work we proved its validity.

Now the accuracy with which the resulting dead MWD of Equation (34) is measured is limited by the resolution of the GPC equipment. Thus the MWD implied by the GPC output reading is

$$\phi_{dead}^{read}(N) = \int_{-\infty}^{\infty} dM \phi_{dead}^{broad}(M) G(N; M) \quad (35)$$

where $G(N; M)$ is the experimental reading (normalized to unity) given a perfectly monodisperse MWD input of chains of length M .

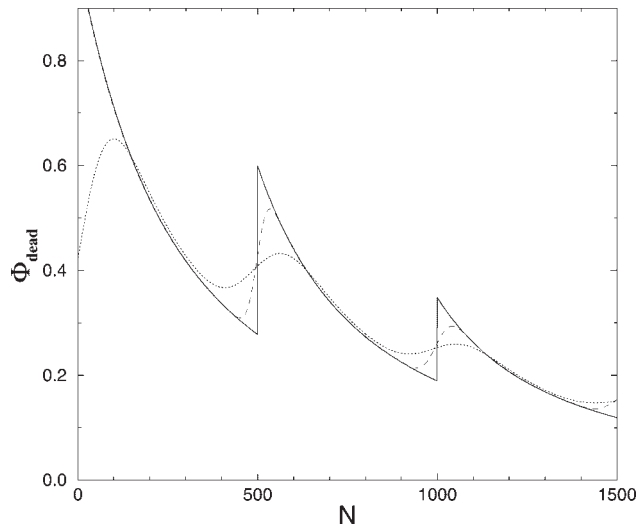


Figure 8. Illustration of dead MWD before and after broadening. The solid line is the unbroadened MWD. The dashed line is the Poisson broadened MWD. The dotted line is the reading on the GPC equipment, given the dashed line as the input MWD. We assumed uniform resolution $\sigma^2 = 5000$ (see main text). Values of parameters used: $v_p = 5000 \text{ s}^{-1}$, $k_c = k_d = 5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $\lambda = 0.1 \text{ s}^{-1}$, $t_0 = 0.1 \text{ s}$, $R_{t0} = 5 \cdot 10^{-7} M$.

Consider values of N near the discontinuity of the unbroadened dead MWD, $N = Ln_0$, and let us examine the location of the inflection point. In the following we will assume that near the discontinuity to leading order G can be approximated by a Gaussian distribution, $G(N; n) = (2\pi\sigma^2)^{-1/2} e^{-(N-n)^2/(2\sigma^2)}$, where σ is a measure of the experimental resolution near Ln_0 . Substituting ϕ_{dead}^{broad} from Equation (34) in Equation (35) one has

$$\begin{aligned} \phi_{dead}^{read}(N) &= \int_{-\infty}^{\infty} dM \phi_{dead}(M) \tilde{\Delta}(N; M), \\ \tilde{\Delta}(N, M) &\equiv \frac{e^{-(N-M)^2/[2(M+\sigma^2)]}}{[2\pi(M+\sigma^2)]^{1/2}} \end{aligned} \quad (36)$$

after using $\int_{-\infty}^{\infty} dP \Delta(P; M) G(N; P) = \tilde{\Delta}(N; M)$ for Gaussian G .

In Appendix H the curvature of ϕ_{dead}^{read} is evaluated close to a discontinuity (Equation (H4)). Setting this to zero one finds two roots, one irrelevant at $\delta N \equiv N - Ln_0 \approx 2(Ln_0 + \sigma^2)$, and one corresponding to the point of inflection at

$$\begin{aligned} \delta N &\approx \left\{ \frac{\phi'_+ - \phi'_-}{\phi_+ - \phi_-} (Ln_0 + \sigma^2) - \frac{1}{2} \right\}, \\ \phi_{+/-} &\equiv \phi_{dead}^{ideal}(Ln_0^{+/-}), \quad \phi'_{+/-} \equiv \frac{d\phi_{dead}^{ideal}}{dN}(Ln_0^{+/-}) \end{aligned} \quad (37)$$

Now in PLP experiments, parameters are normally chosen such that the dead MWD decreases by a factor of order unity

between successive peaks. Hence ϕ'_+ is of order ϕ_+/n_0 and similarly for ϕ_- . Since $\phi'_+ < \phi'_- < 0$ and $\phi_+ > \phi_- > 0$, and taking $L = O(1)$, one has from Equation (37),

$$\delta N \approx -A(1 + B\sigma^2/n_0) \quad (38)$$

where $A, B > 0$ are constants of order unity. This theoretical result is valid provided $n_0^{-1/2} \gg 1$ and β is of order unity. Note that δN is always negative.

Consider first very good experimental resolution, $\sigma \gg n_0^{-1/2}$. In this case the observed broadening is predominantly Poissonian. According to Equation (38), the displacement of the inflection point of the measured MWD away from Ln_0 is then of order one monomer. This is an unimportant correction which is of the same order as the accuracy of the continuum description of the MWD employed in our analysis. We conclude that for this case the inflection point is the appropriate point from which to extract k_p .

Now when $\sigma \gg n_0^{-1/2}$, the broadening of the measured MWD is dominated by the finite experimental resolution. In this case the inflection point is of order $\sigma^2/n_0 \gg 1$ monomers away from Ln_0 . Therefore for large σ , using the location of the inflection point to deduce n_0 leads to a systematic underestimation of v_p . We remark however that this is more accurate than using the local minimum or maximum of the MWD which will then be at a distance of order σ away from n_0 (since we have assumed that $\sigma \ll n_0$, hence $\sigma \gg \sigma^2/n_0$).

As a specific example, consider the experimental MWD of Figure 4. In this Figure, the distance between the local minimum and maximum of the MWD around the inflection point near molecular weight 50 000 ($n_0 \approx 500$) is of order 200 monomers. In this case Poisson broadening would only account for a width $\approx n_0^{1/2} \approx 22$ monomers. Hence broadening appears to be mainly due to limited experimental accuracy and $\sigma \approx 100$. The relative error using the inflection point for the calculation of v_p would then lead to an error of order $\sigma^2/n_0^2 \approx 4\%$.

Conclusions

In this work, we have calculated analytically the number MWD of dead chains produced by pulsed laser polymerization at low conversions. The following effects have been included: living chain termination by both combination and disproportionation; chain transfer of living chain radicals to the environment; broadening effects. Ignoring broadening, we have found the MWD is given by

$$\begin{aligned} \phi_{dead}(N) &= e^{-\lambda N/v_p} \{ \phi_{dead}^{ideal}(N) + \varepsilon \phi_{dead}^{inc}(N) \}, \\ \varepsilon &= \frac{4\lambda\beta t_0}{(1-\beta)^2} \end{aligned} \quad (39)$$

where

$$\begin{aligned} \phi_{dead}^{ideal}(N) &= \text{const.} \left[\frac{k_c}{k} \left\{ (L+1)\beta^L f^2 \left(\frac{rN}{2} \right) + L\beta^{L-1} \right. \right. \\ &\quad \left. \left. \times f^2 \left(\frac{rN+n_0}{2} \right) \right\} + 4 \frac{k_d}{k} \left\{ \frac{\beta^L}{1-\beta} f^2(rN) \right\} \right] \\ \phi_{dead}^{inc}(N) &\equiv \text{const.} \left[\frac{k_c}{k} \left\{ \beta^L [(L+1)\beta - L] + \beta^L (L+1) \right. \right. \\ &\quad \left. \left. \times (1-\beta) f \left(\frac{rN}{2} \right) + L\beta^{L-1} (1-\beta) f \left(\frac{rN+n_0}{2} \right) \right\} \right. \\ &\quad \left. + 2 \frac{k_d}{k} \beta^L f(rN) \right], \quad f(n) \equiv \frac{\beta}{\beta + (1-\beta)n/n_0} \end{aligned} \quad (40)$$

Here $N \equiv Ln_0 + rN$, and “const.” is a normalization constant. The dead MWD is discontinuous at integer multiples of n_0 and is a function of the following independent parameters: n_0 , λt_0 , k_d/k , k_c/k , and β . Here β (see Equation (13)), the fraction of living chains surviving between two successive pulses, is a function of the dimensionless parameter $k\bar{R}_i t_0^2$, where $\bar{R}_i t_0$ is the concentration of new radicals produced per pulse. Equation (39) applies in the limit in which chain transfer is weak, i.e. $\lambda t_0 \ll 1$. Setting $k_c = 0$, Equation (39) reduces to the dead MWD derived in ref.,^[23,24] while setting $\lambda = 0$ one recovers the dead MWD derived in ref.^[6,21]

An important quantity in Equation (39) and (40) is the relative magnitude of the dead MWD discontinuities, shown in Equation (31). Optimally large discontinuities typically correspond to values of β intermediate between zero and unity as has been thoroughly examined by numerical simulations^[11,17] and discussed in ref.^[35] For $\beta \ll 1$ these relative magnitudes are undesirably small. The limit $\beta \rightarrow 1$ (realized when $k\bar{R}_i t_0^2$ is small) may be undesirable also, but this depends on the mode of termination: (i) For the extreme of termination by disproportionation only ($\rho \rightarrow \infty$ in Equation (31)) the discontinuities vanish in this limit while (ii) for termination by combination only ($\rho = 0$) the discontinuities attain their maximum value as $\beta \rightarrow 1$. Thus if combination is strongly dominant, by choosing small R_i this may be a desirable limit (though noise effects are then particularly strong since the absolute amplitude of the dead MWD is very small). In a typical case though where termination occurs by both combination and disproportionation the optimal choice corresponds to intermediate β values.

The effect of chain transfer is to reduce the amplitude of the entire MWD. The amplitude of the discontinuities is reduced by a factor $e^{-\lambda t_0 N/n_0}$. (It follows that if $\lambda t_0 > 1$, most living chains suffer a chain transfer event before growing to a length of order n_0 ; consequently the MWD amplitude at $N = n_0$ is small. Under such conditions PLP is not a useful method for measuring n_0 .) In addition to these effects, transfer introduces an extra “incoherent” contribution to

the dead MWD (see Figure 6) which has no discontinuities and whose magnitude is a fraction λt_0 of the dead MWD.

We have also treated two types of broadening: Poisson and distortion by MWD measuring equipment. Poisson broadening smoothes out the discontinuities of the dead MWD of Equation (39). The broadened dead MWD can be computed by performing numerically the integral of Equation (34). We found that for β of order unity the position of the inflection point of the smooth MWD is not shifted significantly away from the initial discontinuity. (For very small β the inflection point rule leads to underestimation of n_0 .) Thus, if Poisson broadening dominates, then its location can be used reliably to infer k_p .

In practice, the second type of broadening, due to limited GPC resolution, may swamp the Poisson effect. We found that when the band width σ of the GPC output reading, given a perfectly monodisperse sample of degree of polymerization Ln_0 , is much greater than $n_0^{1/2}$, experimental broadening then dominates near the discontinuity at Ln_0 . This leads to a displacement of the point of inflection by approximately σ^2/n_0 monomers below Ln_0 . We remark however that (for β of order unity and $\sigma \ll n_0$) the point of inflection is closer to n_0 than the position of either the minimum or maximum peaks.

Appendix A: Solution to Living Chain Dynamics for Arbitrary $R_i(t)$

In this appendix we solve Equation (6) for general radical production rate $R_i(t)$. Defining $\xi \equiv t - N/v_p$ and $f(\xi, t) \equiv \phi(N, t)$ we have from Equation (6)

$$\left. \frac{\partial f}{\partial t} \right|_{\xi} = -H(t)f + \delta(v_p t - v_p \xi) R_i(t) \quad (A1)$$

with $\phi(N < 0, t) = 0$ implying $f(\xi > t) = 0$. The solution of Equation (A1) is

$$\begin{aligned} f(\xi, t) &= \frac{1}{v_p} \int_{-\infty}^t dt' e^{-\int_{t'}^t H(t'') dt''} \delta(t' - \xi) R_i(t') \\ &= \Theta(t - \xi) \frac{1}{v_p} e^{-\int_{\xi}^t H(t'') dt''} R_i(\xi) \end{aligned} \quad (A2)$$

where Θ is the step function, $\Theta(x > 0) = 1$ and $\Theta(x < 0) = 0$. Hence

$$\phi(N, t) = \frac{\Theta(N)}{v_p} e^{-\int_{t-N/v_p}^t H(t') dt'} R_i(t - N/v_p) \quad (A3)$$

Appendix B: Properties of the Reaction Field $H(t)$

Since $\dot{\Psi} = -H\Psi$ within one cycle (see Equation (9)), it follows that if both t_1 and t_2 belong to the same cycle then

$$e^{-\int_{t_1}^{t_2} H(t') dt'} = \Psi(t_2)/\Psi(t_1), \quad ([t_1] = [t_2]) \quad (B1)$$

Since $\Psi(t)$ drops by a factor β in one cycle of duration t_0 we

also have

$$e^{-\int_{t_1}^{t_2} H(t')dt'} = e^{-\int_{t_1}^{t_2/2} H(t')dt'} e^{-\int_{t_2/2}^{t_2} H(t')dt'} = \frac{\Psi(t_2)}{\Psi(t_1)} \beta^{[t_2]-[t_1]} \quad (\text{B2})$$

after using Equation (B1).

Appendix C: General Expressions for Dead MWD's Generated by Combination

Consider two living MWDs ϕ_1, ϕ_2 which are periodic in time with period t_0 such that ϕ_1 can be written as

$$\phi_1(N, t) = \sum_{j=-\infty}^{\infty} A_1(N) f_1(N - v_p t - j n_0) \quad (\text{C1})$$

where f_1 has period n_0 . Suppose dead chains are generated only by bimolecular reactions involving one 1 and one 2 chain. If only combination reactions occur, the time averaged rate of dead chain generation then satisfies

$$\begin{aligned} \bar{\phi}_{dead}(N) &= \frac{k}{t_0} \int_0^{t_0} dt \int_{-\infty}^{\infty} dM \phi_1(M, t) \phi_2(N - M, t) \\ &= \frac{k}{t_0} \sum_{j=-\infty}^{\infty} \int_0^{t_0} dt \int_{-\infty}^{\infty} dM A_1(M) f_1(M - v_p t - j n_0) \\ &\quad \times \phi_2(N - M, t) = \frac{k}{t_0} \sum_{j=-\infty}^{\infty} \int_{j t_0}^{(j+1)t_0} dt' \\ &\quad \times \int_{-\infty}^{\infty} dM A_1(M) f_1(M - v_p t') \\ &\quad \times \phi_2(N - M, t' + j t_0) \end{aligned} \quad (\text{C2})$$

where we changed variables to $v_p t' = v_p t + j n_0$. We remark that when there is only one chain type reacting with its own type to produce dead chains, then $\phi_1 = \phi_2$ and the rhs of Equation (C2) should be divided by 2. Since ϕ_2 has period t_0 one has the following equivalent expression:

$$\bar{\phi}_{dead}(N) = \frac{k}{t_0} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dM A_1(M) f_1(M - v_p t') \times \phi_2(N - M, t') \quad (\text{C3})$$

With $A_1(N, t) \rightarrow \phi_{env}(N)$, $f_1 \rightarrow \delta$, $\phi_2 \rightarrow \phi_1$, $k \rightarrow k_c$ and dividing by 2 this yields Equation (16) of the main text.

Appendix D: Ideal Case – Combination Part of Dead Chain MWD, Equation (17)

Changing variables $n = 2v_p t + j n_0$ in Equation (16) and using Equation (14) to substitute for ϕ in Equation (16) one has

$$\begin{aligned} \bar{\phi}_{dead}^{comb}(N) &= \frac{k_c}{4v_p t_0} \int_{-\infty}^{\infty} dn \sum_{j=-\infty}^{\infty} \phi_{env}\left(\frac{n + j n_0}{2}\right) \\ &\quad \times \phi_{env}\left(\frac{n - j n_0}{2}\right) \delta(N - n) \\ &= \frac{k_c}{4v_p t_0} \sum_{j=-\infty}^{\infty} \phi_{env}\left(\frac{N + j n_0}{2}\right) \phi_{env}\left(\frac{N - j n_0}{2}\right) \end{aligned} \quad (\text{D1})$$

Writing $N = Ln_0 + rN$, with $L \equiv [N]$, we evaluate the sum of Equation (D1) by noting that since ϕ_{env} is zero for negative values of its arguments, only $-L \leq j \leq L$ contribute. Now using Equation (15) one has

$$\begin{aligned} \phi_{env}\left(\frac{(L+j)n_0 + rN}{2}\right) \phi_{env}\left(\frac{(L-j)n_0 + rN}{2}\right) \\ = \begin{cases} \beta^L \phi_{env}^2(rN/2) & (L-j \text{ even}) \\ \beta^{L-1} \phi_{env}^2((rN + n_0)/2) & (L-j \text{ odd}) \end{cases} \\ (-L \leq j \leq L) \end{aligned} \quad (\text{D2})$$

Noting that the number of even and odd $L-j$ values in the interval $-L \leq j \leq L$ is $L+1$ and L , respectively, and using Equation (D2) and (D1), Equation (17) of the main text is derived after expressing ϕ_{env} in terms of Ψ using Equation (15).

Appendix E: Derivation of Coherent-Incoherent Coupling Term $\bar{\phi}_{dead, cross}^{comb}$

Using Equation (24) and (15), one has from Equation (25) after integrating over the δ -function:

$$\begin{aligned} \bar{\phi}_{dead, cross}^{comb}(N) &= \frac{k_c}{v_p t_0} \int_0^{t_0} dM \phi_{env}(M) \{ \lambda e^{-\lambda N/v_p} \\ &\quad \times \Psi(M/v_p) \beta^{1+[N-2M]+[M]} \} \\ &= \frac{\lambda k_c e^{-\lambda N/v_p}}{v_p t_0} (1 - \beta) \int_0^{t_0} dM \Psi^2(M/v_p) \\ &\quad \times \beta^{L+1+[rN-2rM]} \end{aligned}$$

$$N \equiv Ln_0 + rN, \quad M \equiv Pn_0 + rM \quad (\text{E1})$$

Here we used the identity $-[N - 2M] = [2M - N] + 1$. The integrand of Equation (E1) is independent of P and only depends on the relative magnitude of rN with respect to rM . Since $0 \leq P \leq L$ we may split $\int_0^{t_0}$ into L integrals $\int_0^{rN/2} + \int_{rN/2}^{(rN+n_0)/2} + \int_{(rN+n_0)/2}^{n_0}$ corresponding to $P \leq L-1$, plus the $P=L$ term whose upper integration limit is rN instead of n_0 :

$$\begin{aligned} \bar{\phi}_{dead, cross}^{comb}(N) &= \frac{\lambda k_c e^{-\lambda N/v_p}}{v_p t_0} (1 - \beta) \\ &\quad \times \left\{ (L+1) \beta^{L+1} \int_0^{rN/2} d(rM) \Psi^2(rM/v_p) \right. \\ &\quad + (L+1) \beta^L \int_{rN/2}^{(rN+n_0)/2} d(rM) \Psi^2(rM/v_p) \\ &\quad + L \beta^{L-1} \int_{(rN+n_0)/2}^{n_0} d(rM) \Psi^2(rM/v_p) \\ &\quad \left. + \beta^L \int_{(rN+n_0)/2}^{rN} d(rM) \Psi^2(rM/v_p) \right\} \end{aligned} \quad (\text{E2})$$

The final expression for $\bar{\phi}_{dead,cross}^{comb}$, Equation (26) of the main text, follows from Equation (E2) after using the identity $-k \int_{t_1}^{t_2} dt \Psi^2 = \Psi(t_2) - \Psi(t_1)$ for $0 < t_1, t_2 < t_0$.

Appendix F: Disproportionation and Chain Transfer Contribution to Dead MWD

From Equation (24), the time average of ϕ_{coh} is

$$\bar{\phi}_{coh}(N) = \frac{1}{v_p t_0} e^{-\lambda N/v_p} \phi_{env}(N) \quad (F1)$$

Hence using the definition of ϕ_{env} (Equation (15)) and $\dot{\Psi}(t) = -k\Psi^2(t)$ for $0 < t < t_0$,

$$-v_p \frac{\partial \bar{\phi}_{coh}}{\partial N} = \frac{1}{v_p t_0} e^{-\lambda N/v_p} \phi_{env}(N) [\lambda + k\Psi(rN/v_p)] \quad (F2)$$

The time average of ϕ_{inc} is calculated after integrating the 3rd expression in Equation (24) from 0 to t_0 . The value of the integrand depends on the relative magnitudes of rN/v_p and t :

$$\bar{\phi}_{inc}(N) = \frac{\lambda e^{-\lambda N/v_p}}{v_p t_0} \beta^{[N]+1} \left\{ \int_0^{rN/v_p} dt \Psi(t) + \frac{1}{\beta} \int_{rN/v_p}^{t_0} dt \Psi(t) \right\} \quad (F3)$$

Hence neglecting terms proportional to λ^2 ,

$$-v_p \frac{\partial \bar{\phi}_{inc}}{\partial N} = \frac{1}{v_p t_0} \lambda e^{-\lambda N/v_p} \phi_{env}(N) + O(\lambda^2) \quad (F4)$$

Thus from Equation (F1)–(F4) one has

$$-\frac{k_d}{k} v_p \frac{\partial \bar{\phi}}{\partial N} + \frac{k_c}{k} \lambda \bar{\phi}(N) = C e^{-\lambda N/v_p} \times \left\{ 4 \frac{k_d \beta^{[N]}}{k(1-\beta)} f^2(rN) + \varepsilon \left(2 \frac{k_d}{k} + \frac{k_c}{k} \right) \beta^{[N]} f(rN) \right\} \quad (F5)$$

after using Equation (15) and (18) and the definition of ε in Equation (29). Here we neglected $O(\lambda^2)$ terms.

Appendix G: Poisson Broadening of Living MWD: Derivation of Equation (33)

In order to include broadening effects in the living dynamics, a “diffusion” term must be added in Equation (6) and (22) as follows:

$$\dot{\phi}_{broad} = -v_p \frac{\partial \phi_{broad}}{\partial N} + \frac{v_p}{2} \frac{\partial^2 \phi_{broad}}{\partial N^2} - \tilde{H}(t) \phi + \tilde{R}_i(t) \delta(N) \quad (G1)$$

where $\tilde{H}(t) \equiv H(t) + \lambda$ and $\tilde{R}_i \equiv R_i(t) + \lambda\Psi(t)$. In the absence of the last two sink and source terms, Equation (G1) describes the evolution of the probability distribution function a unidirectional walk with step size unity and velocity v_p , in the continuum limit. The diffusion coefficient for such a walk^[36] is $v_p/2$.

Now in the absence of the source and sink terms, the propagator of Equation (G1) for a pulse generated at $N=0$

at $t=0$, is simply $\Delta(N; v_p t)$. (Here we neglected the condition $\phi_{broad}(N < 0; t) = 0$ which implies that the propagator be zero for negative N values. However for $v_p t > 1$, the amplitude of $\Delta(N; v_p t)$ becomes exponentially small for negative N . This implies that the use of Δ is a very good approximation provided we examine the living MWD for $N \gg 1$.) Hence the solution of Equation (G1) is

$$\phi_{broad}(N, t) = \int_{-\infty}^t dt' e^{-\int_{t'}^t \tilde{H} R_i(t'') \Delta(N; v_p(t-t'))} \quad (G2)$$

This solution is identical to the solution of the unbroadened living MWD in Equation (A2), after replacing $\delta(t' - \xi) = v_p \delta(N - v_p(t-t'))$ in Equation (A2) by $\Delta(N; v_p(t-t'))$. Hence Equation (33) follows immediately as one may check after replacing ϕ from Equation (A2) into Equation (33) and checking that Equation (G2) is recovered.

Appendix H: Curvature of Broadened Dead MWD Near the Point of Inflection

Considering molecular weights near Ln_0 , expanding $\phi_{dead}(n)$ one has (see Equation (37) for notation)

$$\begin{aligned} \phi_{dead}(n) &= (\phi_+ + \phi'_+ \delta n + \dots) \Theta(\delta n) \\ &\quad + (\phi_- + \phi'_- \delta n + \dots) \Theta(-\delta n), \\ \delta n &\equiv n - Ln_0 \end{aligned} \quad (H1)$$

Since the amplitude of the unbroadened dead MWD decreases smoothly by a factor of order unity between successive peaks, the magnitude of ϕ'_+ is of order ϕ_+/n_0 , and similarly for ϕ'_- . Now since the δn which will survive in the integration of Equation (34) around $N \approx Ln_0$ is of order $\Sigma \equiv (Ln_0 + \sigma^2)^{1/2}$, Equation (H1) is an expansion up to order Σ/n_0 . Approximating $\tilde{\Delta}$ with a Gaussian of fixed width, and keeping terms up to order $1/\Sigma$ (note $\Sigma/n_0 \geq 1/\Sigma$):

$$\begin{aligned} \tilde{\Delta}(N; n) &= \frac{1}{(2\pi\Sigma^2)^{1/2}} e^{-(\delta N - \delta n)^2 / (2\Sigma^2)} \\ &\quad \times \left\{ 1 - \frac{\delta n}{2\Sigma^2} + \frac{\delta n(\delta N - \delta n)^2}{2\Sigma^4} + \dots \right\}, \\ \delta N &\equiv N - Ln_0 \end{aligned} \quad (H2)$$

Substituting Equation (H1) and (H2) in Equation (34) we obtain the following approximation to the MWD output reading near Ln_0 :

$$\begin{aligned} \phi_{dead}^{read}(N) &= \frac{1}{(2\pi\Sigma^2)^{1/2}} \int_0^\infty d(\delta n) \left\{ \phi_+ + \delta n \right. \\ &\quad \times \left(\phi'_+ - \frac{\phi_+}{2\Sigma^2} + \frac{\phi_+(\delta N - \delta n)^2}{2\Sigma^4} \right) \left. \right\} e^{-(\delta N - \delta n)^2 / (2\Sigma^2)} \\ &\quad + \frac{1}{(2\pi\Sigma^2)^{1/2}} \int_{-\infty}^0 d(\delta n) \{ \dots \}_{\phi_+, \phi'_+ \rightarrow \phi_-, \phi'_-} \end{aligned} \quad (H3)$$

A straightforward differentiation of Equation (H3) gives

$$\frac{d^2 \phi_{dead}^{read}}{dN^2} = \frac{1}{(2\pi\Sigma^2)^{1/2}} \left\{ \phi'_+ - \phi'_- + \frac{\phi_- - \phi_+}{2\Sigma^2} \right. \\ \left. \times \left[1 + 2\delta N - \frac{(\delta N)^2}{\Sigma^2} \right] \right\} e^{-(\delta N)^2/(2\Sigma^2)} \quad (\text{H4})$$

Acknowledgement: This work was supported by the *National Science Foundation* under grant no. DMR-9816374. We thank *Erdem Karatekin* for illuminating discussions.

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