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# Conditions for the Determination of Precise and Accurate Free-Radical Propagation Rate Coefficients from Pulsed-Laser-Made Polymer

**Jürgen Sarnecki and Johannes Schweer***

*Bayer AG, Central Research and Development, D-51368 Leverkusen, Germany*

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ABSTRACT: A revision of the long known mathematical representation of the chain length distribution of polymer resulting from pulsed-laser-initiated free-radical polymerization of Aleksandrov, Genkin, Kitai, Smirnova, and Sokolov revealed that it vividly reflects some very essential characteristics of the underlying kinetics, which have so far been largely overlooked. In particular, with respect to an experimental determination of the propagation rate coefficient $k_p$, it was found that this representation suggests the measurement of the chain lengths at maxima or at low molecular weight side inflection points of pulsed initiation originating structures within chain length distributions of pulsed-laser-made polymer, depending on whether sufficiently high or low concentrations of radicals are being produced per initiating laser pulse, respectively. This suggestion was verified for pulsed laser polymerizations of styrene and methyl methacrylate, at which values of $k_p$(styrene) = 92 L mol$^{-1}$ s$^{-1}$ and $k_p$ (methyl methacrylate) = 359 L mol$^{-1}$ s$^{-1}$ were obtained for a temperature of 25 °C.

## Introduction

The determination of free-radical propagation rate coefficients $k_p$ from molecular weight distributions of pulsed-laser-made polymer has received explicit recommendation[1] for being unusually reliable. It seems to be unaffected by almost all shortcomings which have until now been common to experimental efforts to obtain individual kinetic rate coefficients for free-radical polymerizations like, for instance, unknown initiator efficiency, unknown conversion, solvent, and chain-length dependence of kinetic parameters, unknown mode of the termination reaction, unknown amount of termination by oxygen or "impurities", etc.

The pulsed-laser polymerization method was invented as a combination of a pulsed-laser polymerization (PLP) and a determination of the molecular weight distribution (MWD) or the equivalent chain length distribution (CLD) of the resultant polymer via size exclusion chromatography (SEC) by Olaj et al.[2] Essentially, this technique comes down to a measurement of chain lengths

$$i_T = k_p c_M T \qquad (1)$$

from structured CLDs (MWDs) of pulsed-laser-made polymer, where the chain lengths $i_T$ correspond to polymer molecules that have grown over an integer multiple of the time intervall $T$ between successive laser pulses. Beyond the propagation rate coefficient $k_p$, eq 1 contains only two more parameters which are, however, accurately known, measurable, or controlable: $T$ can usually be exactly set by the pulse repetition rate control of the laser; the molar concentration of monomer $c_M$ is generally known or can easily be measured and, as far as soluble material is concerned, also the polymer's molecular weight can usually be measured fairly accurately by modern SEC equipment. Thus the determination of $k_p$ from

$$k_p = i_T/(c_M T) \qquad (2)$$

is very straightforward. With respect to its simplicity and accuracy, the PLP method continues to acquire increasing scientific as well as technical interest and application. With special respect to its high power of obtaining "absolute" or "individual" rate coefficients, it seems legitimate to characterize it as "a key free-radical polymerization kinetics experiment". Classical experimental techniques of studying free-radical polymerization kinetics do not usually yield individual values of rate coefficients but rate parameters that are composed of at least two or even more individual rate coefficients.

The present paper is intended to aid experimental design toward achieving reliable determination of accurate and precise values of $k_p$ using the PLP method and to draw attention back to some pioneering work on pulsed-laser polymerization kinetics: Although it was only in 1987 that Olaj et al. proposed the application of the PLP "...as a tool of evaluating (individual) kinetic constants of free-radical polymerization...",[2] it was more than 10 years earlier that Aleksandrov, Genkin, Kitai, Smirnova, and Sokolov studied the "kinetics of laser initiated polymerization" in considerable detail and derived a closed form expression for "...the molecular weight distribution of the resultant polymer",[3] which appears to be quite correct and at the same time quite helpful in understanding qualitatively the radical growth and polymer buildup during pulsed-laser-initiated free-radical polymerizations.

## Model

The mathematical function describing the CLD of polymer "formed by pulse-periodic initiation" of free-radical polymerization according to Aleksandrov et al.[3] reads

$$w(i) = i \sum_{N=n^*}^{\mathrm{Int}(t/T)} c_{\mathrm{R},0}^{0} \int_0^{\tau} \sum_{n=0}^{2n^*} \frac{p_c + p_d}{{t_T}^n {t_{\tau'}}^2}\, \mathrm{d}\tau' \qquad (3)$$

where

$$t_{\tau'} = 1 + k_t c_R^{\max} \tau' \qquad (3a)$$

$$t_T = 1 + k_t c_R^{\max} T \qquad (3b)$$

$$p_c = k_{tc} c_{\mathrm{R},0}^{0} \frac{\exp\left(-\dfrac{k_p c_M^N (nT + 2\tau')}{1 - k_p/k_t}\right)\left(\dfrac{k_p c_M^N (nT + 2\tau')}{1 - k_p/k_t}\right)^i}{i!} \qquad (3c)$$

and

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$$p_{\mathrm{d}} = k_{\mathrm{td}} c_{\mathrm{R}}^{\max} \frac{\exp\left(-\dfrac{k_{\mathrm{p}} c_{\mathrm{M}}^{N}(nT+\tau')}{1-k_{\mathrm{p}}/k_{\mathrm{t}}}\right)\left(\dfrac{k_{\mathrm{p}} c_{\mathrm{M}}^{N}(nT+\tau')}{1-k_{\mathrm{p}}/k_{\mathrm{t}}}\right)^{i}}{i!} \tag{3d}$$

It accounts for second-order radical propagation and termination, the latter being possible in the combination and in the disproportionation mode. The parameters contained in eqs 3 are summarized in Table 1. The CLD, i.e. the weight fraction *w(i)* of polymer of chain length *i* as a function of chain length *i*, is essentially expressed as an integral over the continuous time variable $\tau'$, which ranges from time zero to the time $T$ between two successive laser pulses. The upper integration limit $\tau$ is to be set equal to $T$, if—as will be the usual case—the complete CLD is considered. It may however also be set to some fraction of $T$, if—as will be shown below—the development of *w(i)* up to that fraction of $T$ is considered. Within the derivation of eq 3, "pulsed" initiation is understood to mean that laser pulses are used "whose duration is much less than the characteristic time needed for the attachment of a molecule to a growing monomer chain ($10^{-4}$ s)", thus allowing us "to regard initiation as an instantaneous process" which "simplifies greatly the analysis of the polymerization kinetics".[3]

The integral in eq 3 contains a series of Poisson distribution terms $p_{\mathrm{c}}$ and $p_{\mathrm{d}}$ located at expectation values $(k_{\mathrm{p}}c_{\mathrm{M}}^{N}(nT + 2\tau'))/(1 - k_{\mathrm{p}}/k_{\mathrm{t}})$ or $(k_{\mathrm{p}}c_{\mathrm{M}}^{N}(nT + \tau'))/(1 - k_{\mathrm{p}}/k_{\mathrm{t}})$, as far as termination by combination and disproportionation is concerned, respectively. It is assumed that the pseudo steady state, which is reached after $n^*$ pulses and which is characterized by the "steady-state concentration" $c_{\mathrm{R}}^{\max}$ of radicals at $\tau' = 0$, has been achieved; $c_{\mathrm{R,0}}^{0}$ is the radical concentration of chain length zero generated per laser pulse at $\tau' = 0$ which will hereafter be referred to as the start concentration of radicals; $c_{\mathrm{M}}^{N}$ is the monomer concentration $c_{\mathrm{M}}$ after $N$ pulses which means that eq 3 automatically accounts for an eventual decrease of $c_{\mathrm{M}}$ during polymerization. Absolute values of the termination rate coefficients contained in eq 3 refer to the definition of the rate of termination as $-\mathrm{d}c_{\mathrm{R}}/\mathrm{d}t = k_{\mathrm{t}}c_{\mathrm{R}}^{2}$, where $c_{\mathrm{R}}$ is the total concentration of radicals.

Within the present investigation, the main aim is to illustrate eq 3 to aid the qualitative understanding of how radical growth and polymer formation proceed, when "pulse-periodic" initiation is applied to free-radical polymerization systems. With respect to further details and to the deviation of eq 3 we will thus restrict ourselves to referring to the original literature.

## Model Calculations

Equation 3 can easily be evaluated by numerical integration. Corresponding results of *w(i)* for a model system, which, as far as kinetic parameters are concerned, is fairly close to the situation of the free-radical polymerization of bulk styrene at 25 °C (see for instance ref 4), are shown in Figure 1 (upper section) together with numerically obtained derivatives d*w(i)*/d*i* (middle section), which have also been plotted on an expanded scale (lower section). All curves in Figure 1 refer to the same scale of chain length *i*.

The fine curves in Figure 1 were obtained for a calculation with $c_{\mathrm{R,0}}^{0} = 10^{-7}$ mol L$^{-1}$. The suggestion of Olaj et al.[2] to identify characteristic inflection points within CLDs of pulsed-laser-made radical polymer with the quantity $i_T$ is clearly evident from the corresponding plot of d*w(i)*/d*i* against *i*, which shows maxima (i.e. inflection points of *w(i)*) obviously coinciding exactly with the calculation input for integer multiples of $i_T$. Values of the 1-, 2-, 3-, and 4-fold multiples of $i_T$ are indicated as dotted vertical lines at $i$ = 100, 200, 300, and 400 in Figure 1. Propagation and termination rate coefficients were regarded as constants throughout the present investigation, as the monomer conversions were considered to be always low.[3]

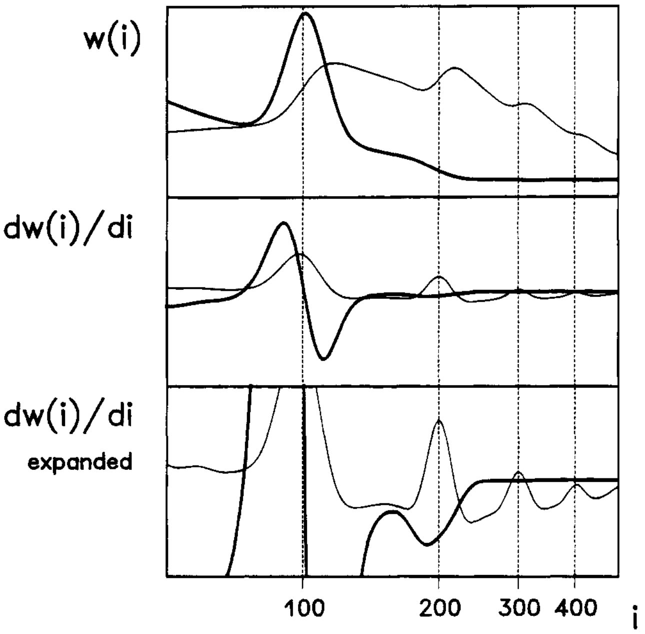

**Figure 1.** Calculations of the weight fraction *w(i)* of polymer of chain length *i* according to eq 3 and numerical differentiations d*w(i)*/d*i* thereof: (bold curves) $c_{\mathrm{R,0}}^{0} = 10^{-5}$ mol L$^{-1}$; (fine curves) $c_{\mathrm{R,0}}^{0} = 10^{-7}$ mol L$^{-1}$ ($k_{\mathrm{p}} = 100$ L mol$^{-1}$ s$^{-1}$, $c_{\mathrm{M}}^{N}$ = constant = 10 mol L$^{-1}$, $T = 0.1$ s, $k_{\mathrm{tc}} = 10^{8}$ L mol$^{-1}$ s$^{-1}$, $k_{\mathrm{td}} = 10^{7}$ L mol$^{-1}$ s$^{-1}$, Int($t/T$) = $n^*$ = 5, values of ordinates were plotted in arbitrary units against chain length *i*). Values of $i_T$ and integral multiples thereof are indicated as dotted vertical lines.

**Table 1. Parameters Contained in Eq 3**

| parameter | meaning | units |
|---|---|---|
| $t$ | polymerization time | s |
| $T$ | time between two successive laser pulses | s |
| $\tau, \tau'$ | continuous time variables ranging from 0 to $T$ | s |
| $i$ | kinetic chain length | |
| $n, N$ | number of laser pulses | |
| $c_{\mathrm{R,0}}^{0}$ | concentration of radicals of chain length 0 produced per laser pulse at $\tau' = 0$; "start concentration of radicals" | mol L$^{-1}$ |
| $c_{\mathrm{R}}^{\max}$ | maximum concentration of radicals, i.e. concentration at $\tau' = 0$ when the pseudo steady state has been reached; "steady-state concentration of radicals": $c_{\mathrm{R}}^{\max} = c_{\mathrm{R,0}}^{0}/2 + (c_{\mathrm{R,0}}^{0\,2}/4 + c_{\mathrm{R,0}}^{0}/(k_{\mathrm{t}}T))^{1/2}$ | mol L$^{-1}$ |
| $n^*$ | number of laser pulses, after which $c_{\mathrm{R}}^{\max}$ is reached | |
| $\kappa(n)$ | $\kappa(n) = n/2 + 1$ for even $n$; $\kappa(n) = (n + 1)/2$ for odd $n$ | |
| $c_{\mathrm{M}}^{N}$ | monomer concentration at pulse $N$ | mol L$^{-1}$ |
| $k_{\mathrm{p}}$ | propagation rate coefficient | L mol$^{-1}$ s$^{-1}$ |
| $k_{\mathrm{tc}}$ | termination rate coefficient, combination | L mol$^{-1}$ s$^{-1}$ |
| $k_{\mathrm{td}}$ | termination rate coefficient, disproportionation | L mol$^{-1}$ s$^{-1}$ |
| $k_{\mathrm{t}}$ | $k_{\mathrm{t}} = k_{\mathrm{td}} + k_{\mathrm{tc}}$ | L mol$^{-1}$ s$^{-1}$ |

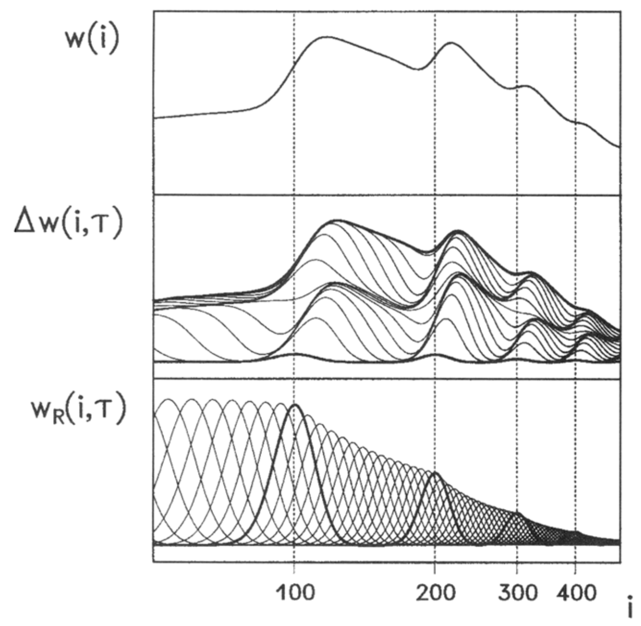

**Figure 2.** Upper section: calculation of the weight fraction *w(i)* of polymer of chain length *i* corresponding to a numerical integration of eq 3 up to $\tau = T$. Middle section: calculation of a fraction $\Delta w(i,\tau)$ of the weight fraction of polymer of chain length *i* corresponding to a numerical integration of eq 3 up to successively increased fractions $\tau$ of *T* starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms. Bold curves correspond to $\Delta w(i,0)$ and $\Delta\tau' \approx 1$ ms (bottom) and $\Delta w(i,T)$ (top), respectively. Lower section: calculation of the weight fraction $w_R(i,\tau)$ of radicals of chain length *i* at successively increased fractions $\tau$ of *T* according to eq 4 starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms using $k_t = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$. Bold curves correspond to $w_R(i,0)$ as well as to $w_R(i,T)$. ($k_p = 100$ L mol$^{-1}$ s$^{-1}$, $c_M^N$ = constant = 10 mol L$^{-1}$, $T = 0.1$ s, $k_{tc} = 10^8$ L mol$^{-1}$ s$^{-1}$, $k_{td} = 10^7$ L mol$^{-1}$ s$^{-1}$,$c^0_{R,0} = 10^{-7}$ mol L$^{-1}$, Int($t/T$) = $n^* = 5$, values of ordinates were plotted in arbitrary units against chain length *i*.) Values of $i_T$ and integral multiples thereof are indicated as dotted vertical lines.

The bold curves in Figure 1 were calculated with $c^0_{R,0} = 10^{-5}$ mol L$^{-1}$. The inflection points are obviously no longer the right measures of the value of $i_T$ in this case, but now the maximum of *w(i)* appears in its immediate proximity; i.e. d*w(i)*/d*i* is close to zero at this chain length (middle section of Figure 1). There is obviously only one dominant pulsed initiation originating (PIO) peak in this case, so that a look at the expanded scale of d*w(i)*/d*i* in Figure 1 consequently reveals that the structure of the CLDs derivative, which appears around $i = 100$ in the middle section of Figure 1, is not repeated a second or even a third time (bold curve), as is obviously the case with the $c^0_{R,0} = 10^{-7}$ mol L$^{-1}$ calculation (fine curve). However a minimum appears at roughly $2i_T$. The origin of this phenomenon as well as the shift of the correct measure of $i_T$ from the low molecular weight side inflection point of PIO structures to the maximum of PIO peaks when progressing, for instance, from low to high values of start concentrations of radicals will be considered below. The possibility of creating "very high concentrations of initiating radicals ($10^{-4}$–$10^{-6}$ mole/liter)" by means of the high power densities of laser radiation pulses was already indicated by Aleksandrov et al.[3] Due to the advent of modern high-power excimer pulse lasers, the production of concentrations of initiating radicals of the order of $10^{-5}$ mol L$^{-1}$ may nowadays be taken "as a matter of course". Within the present investigation, energies of laser pulses (or of radical concentrations thereby produced) are called "low" or "high" with respect to the experimental conditions under which inflection points or maxima within CLDs of pulsed-laser-made polymer measure $i_T$, respectively.

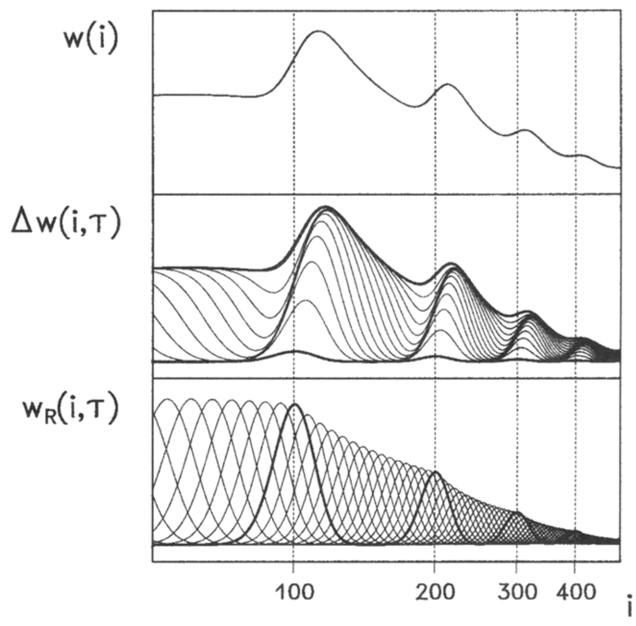

**Figure 3.** Upper section: calculation of the weight fraction *w(i)* of polymer of chain length *i* corresponding to a numerical integration of eq 3 up to $\tau = T$. Middle section: calculation of a fraction $\Delta w(i,\tau)$ of the weight fraction of polymer of chain length *i* corresponding to a numerical integration of eq 3 up to successively increased fractions $\tau$ of *T* starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms. Bold curves correspond to $\Delta w(i,0)$ and $\Delta\tau' \approx 1$ ms (bottom) and $\Delta w(i,T)$ (top), respectively. Lower section: calculation of the weight fraction $w_R(i,\tau)$ of radicals of chain length *i* at successively increased fractions $\tau$ of *T* according to eq 4 starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms using $k_t = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$. Bold curves correspond to $w_R(i,0)$ as well as to $w_R(i,T)$. ($k_p = 100$ L mol$^{-1}$ s$^{-1}$, $c_M^N$ = constant = 10 mol L$^{-1}$, $T = 0.1$ s, $k_{tc} = 0$ L mol$^{-1}$ s$^{-1}$, $k_{td} = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$, $c^0_{R,0} = 10^{-7}$ mol L$^{-1}$, Int($t/T$) = $n^* = 5$, values of ordinates were plotted in arbitrary units against chain length *i*.) Values of $i_T$ and integral multiples thereof are indicted as dotted vertical lines.

To illustrate the formation of polymer as a function of time after a laser pulse, eq 3 was integrated up to different fractions $\tau$ of the full pulse period *T* (in steps of $\Delta\tau$ of approximately 6.7 ms, starting from $\tau = 0$) using $c^0_{R,0} = 10^{-7}$ mol L$^{-1}$ together with the parameter set corresponding to Figure 1 (middle section of Figure 2): Bold curves refer to $\Delta w(i,0)$ and $\Delta w(i,T)$. The distribution $\Delta w(i,0)$, which actually represents the integration of eq 3 up to $\tau = 0$, should theoretically be zero at all chain lengths. Because the numerical integration was performed over finite intervals of $\Delta\tau' \approx 1$ ms, a small amount of polymer is calculated even at $\tau = 0$, thus effectively illustrating the chain length intervals at which polymer formation starts. In Figure 2 it actually starts simultaneously at chain lengths of $jk_pc_MT$ at $\tau = 0$ ($j = 0, 1, 2, ...$) and extends essentially up to chain lengths of approximately $(j + 2)k_pc_MT$ each time. This behavior is a consequence of choosing $k_{tc}$ 10 times greater than $k_{td}$, i.e. choosing combination-dominated termination. The integration of eq 3 up to *T* is replotted in the upper section of Figure 2 for the purpose of direct comparison.

Figure 3 shows a calculation in which, besides zero termination by combination, $k_{td}$ was chosen as $1.1 \times 10^8$

L mol$^{-1}$ s$^{-1}$ and where all other model parameters were left unchanged with respect to Figure 2. In this case the polymer formation again starts simultaneously at chain lengths of $jk_pc_MT$ at $\tau = 0$ ($j = 0, 1, 2, ...$) but extends essentially only up to chain lengths of approximately $(j + 1)k_pc_MT$ in each case. Despite this difference, the general character of the calculated full CLDs in the upper sections of Figures 2 and 3 does not appear to show any major modification when changing from a combination-type to a disproportionation-type of termination. It might be noted in passing that a very slightly enhanced "smearing out" of PIO structures due to predominant termination by combination may be observed in Figure 2 as compared to Figure 3. This finding matches up well with statements already given by Olaj et al.[2] and others,[5] but contrasts for instance with the suggestion of Lu et al.[6] who essentially suggested that $i_T$ should in practice be more easily locatable for a "system which is dominated by a combination-type of termination".

Figures 2 and 3 also contain illustrations of the weight fraction $w_R(i,\tau)$ of radicals of chain length $i$ at successively increased fractions $\tau$ of $T$ (again starting at $\tau = 0$, step width of $\Delta\tau$ of approximately 6.7 ms), which were approximated according to

$$w_R(i,\tau) = ic^0_{R,0}\sum_{n=0}^{2n^*}\frac{p_t}{t_T^{\,n}t_\tau} \tag{4}$$

where

$$t_\tau = 1 + k_tc_R^{\max}\tau \tag{4a}$$

$$t_T = 1 + k_tc_R^{\max}T \tag{4b}$$

and

$$p_t = k_tc_R^{\max}\frac{\exp\left(-\dfrac{k_pc_M^N(nT+\tau)}{1-k_p/k_t}\right)\left(\dfrac{k_pc_M^N(nT+\tau)}{1-k_p/k_t}\right)^i}{i!} \tag{4c}$$

with $k_t = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$ each time. Equation 4 was extracted from eq 3 by assuming that the CLD of radicals corresponds to the instantaneous CLD of polymer formed via termination by disproportionation. The resulting expression for the CLD of growing radicals (which holds for chain-length-independent termination) does not depend on the mode of termination. As, besides all other parameters, the same overall $k_t$ was used for its evaluation, the corresponding illustrations in Figures 2 and 3 ought to be identical. Bold curves correspond to calculations of $w_R(i,0)$, which are identical to calculations of $w_R(i,T)$ and which respresent the CLDs of radicals at exactly the same instant as a new $c^0_{R,0}$ is established. Single peaks in these curves measure the weight fraction of radicals which survived the number of initiating pulses equal to integer quotients of their Poisson-broadened chain lengths and $i_T$.

For the parameters used for the calculations of Figures 2 and 3, termination proceeds relatively slowly. Moreover the decrease of $w_R(i,\tau)$ with time due to second-order termination is partly counterbalanced by radical growth. Thus a significant weight fraction of radicals may reach chain lengths of $i > 400$. In eq 3 these findings are expressed by the number of pulses $n^*$, after which the pseudo steady state of radicals is reached or, in other words, which a significant fraction of growing radicals may survive, when their birth pulse is considered as number zero. For the parameter set under consideration, $n^*$ was determined[7] as 5 to within good approximation. Thus, although amplified by radical growth, the weight fraction of radicals at a chain length corresponding to 5 pulse periods of growth is already small. Of course, analogous considerations apply with respect to polymer formation; i.e., within the framework of eq 3, the number of laser pulses, which a significant amount of growing radicals may survive, essentially governs the molecular weight limit up to which polymer chains may be formed.

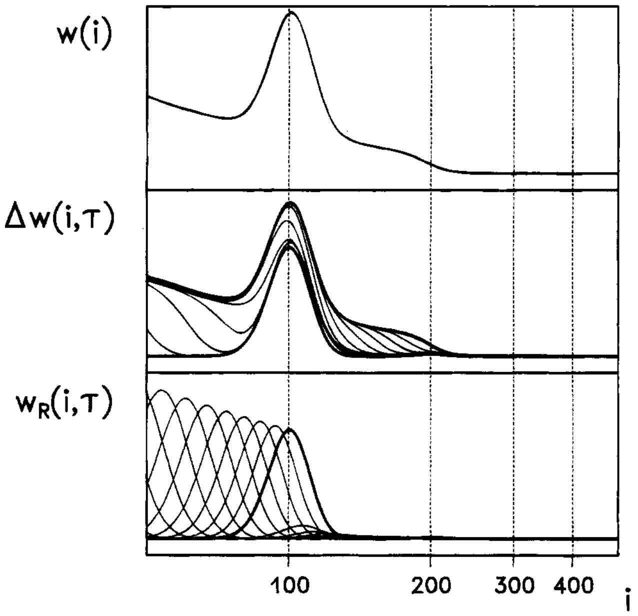

**Figure 4.** Upper section: calculation of the weight fraction $w(i)$ of polymer of chain length $i$ corresponding to a numerical integration of eq 3 up to $\tau = T$. Middle section: calculation of a fraction $\Delta w(i,\tau)$ of the weight fraction of polymer of chain length $i$ corresponding to a numerical integration of eq 3 up to successively increased fractions $\tau$ of $T$ starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms. Bold curves correspond to $\Delta w(i,0)$ and $\Delta\tau' \approx 1$ ms (bottom) and $\Delta w(i,T)$ (top), respectively. Lower section: calculation of the weight fraction $w_R(i,\tau)$ of radicals of chain length $i$ at successively increased fractions $\tau$ of $T$ according to eq 4 starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms using $k_t = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$. The bold curve corresponds to $w_R(i,0)$ as well as to $w_R(i,T)$. ($k_p = 100$ L mol$^{-1}$ s$^{-1}$, $c_M^N$ = constant = 10 mol L$^{-1}$, $T = 0.1$ s, $k_{tc} = 10^8$ L mol$^{-1}$ s$^{-1}$, $k_{td} = 10^7$ L mol$^{-1}$ s$^{-1}$, $c^0_{R,0} = 10^{-5}$ mol L$^{-1}$, Int$(t/T) = n^* = 2$, values of ordinates were plotted in arbitrary units against chain length $i$.) Values of $i_T$ and integral multiples thereof are indicted as dotted vertical lines.

When the start concentration of radicals is raised from $c^0_{R,0} = 10^{-7}$ mol L$^{-1}$ to $10^{-5}$ mol L$^{-1}$, the graphs of Figures 4 and 5 result, which have been calculated analogously to the curves shown in Figures 2 and 3. Inspection of the time-resolved calculation of the development of the CLDs of polymer and growing radicals in the middle and lower sections of Figures 4 and 5 immediately reveals that the location of the PIO peak in the final CLD (upper sections of Figure 4 and 5) is already basically fixed by the CLD of growing radicals at $\tau = 0$, which implies that it is predominantly the peaks maximum which is the right measure of $i_T$ (see Figure 1 for comparison). As in Figures 2 and 3, bold curves in the middle and lower sections of Figures 4 and 5 again represent distributions referring to time $\tau = 0$ or $\tau = T$, respectively. It was already mentioned that,

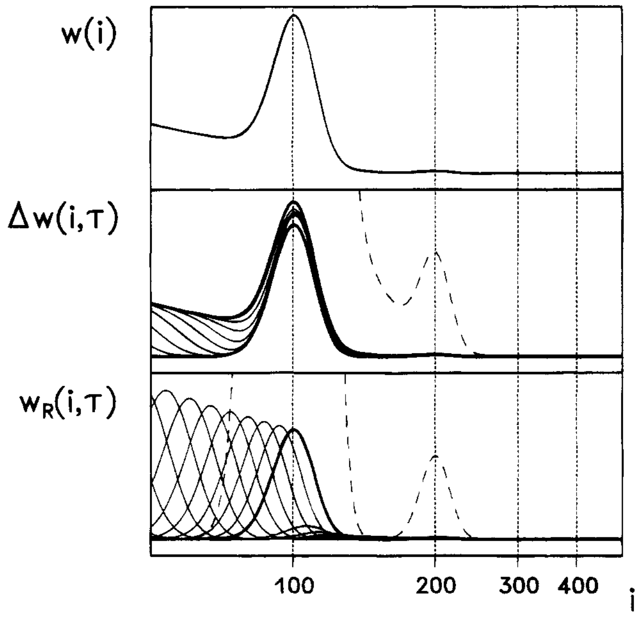

**Figure 5.** Upper section: calculation of the weight fraction $w(i)$ of polymer of chain length $i$ corresponding to a numerical integration of eq 3 up to $\tau = T$. Middle section: calculation of a fraction $\Delta w(i,\tau)$ of the weight fraction of polymer of chain length $i$ corresponding to a numerical integration of eq 3 up to successively increased fractions $\tau$ of $T$ starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms. Bold curves correspond to $\Delta w(i,0)$ and $\Delta\tau' \approx 1$ ms (bottom) and $\Delta w(i,T)$ (top), respectively. Lower section: calculation of the weight fraction $w_R(i,\tau)$ of radicals of chain length $i$ at successively increased fractions $\tau$ of $T$ according to eq 4 starting from $\tau = 0$ in steps of $\Delta\tau$ of approximately 6.7 ms using $k_t = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$. The bold curve corresponds to $w_R(i,0)$ as well as to $w_R(i,T)$. The distributions $\Delta w(i,T)$ and $w_R(i,T)$ have been replotted on an expanded scale (broken curves). ($k_p = 100$ L mol$^{-1}$ s$^{-1}$, $c_M^N$ = constant = 10 mol L$^{-1}$, $T = 0.1$ s, $k_{tc} = 0$ L mol$^{-1}$ s$^{-1}$, $k_{td} = 1.1 \times 10^8$ L mol$^{-1}$ s$^{-1}$, $c_{R,0}^0 = 10^{-5}$ mol L$^{-1}$, Int$(t/T) = n^* = 2$, values of ordinates were plotted in arbitrary units against chain length $i$.) Values of $i_T$ and integral multiples thereof are indicted as dotted vertical lines.

for the reason of numerical integration of eq 3 over finite intervals of time, the calculations of $\Delta w(i,0)$, which appear as the bottom curves in the middle sections of Figures 4 and 5, actually represent the polymer formed within a time intervall $\Delta\tau' \approx 1$ ms, right after the arrival of an initiating pulse. It is therefore comprehensible not only that the peak in the final CLD is predominantly determined by $w_R(i,0)$ but also that it is obviously a prerequisite, that this determination be completed within a small fraction of $T$, because otherwise a shift in the peak position due to radical growth should occur; i.e., the peak position in the final CLD would then no longer be predominantly determined by $w_R(i,0)$. The importance of considering radical termination and growth reactions occurring in parallel is again evident from representations of $w_R(i,\tau)$ in the lower sections of Figures 4 and 5: Starting from the distribution $w_R(i,0)$, which is present at the instant when a new $c_{R,0}^0$ is established (bold curves), the weight fraction of growing radicals rapidly drops to very low values almost within the width of $w_R(i,0)$. In view of a comparison of Figures 2 and 3 on the one hand, where termination of growing radicals was seen to proceed relatively slowly, and Figures 4 or 5 on the other hand, where termination of growing radicals obviously proceeds much more rapidly in comparison to their growth, the obvious thing is to try and trace the origin of these findings back to the kinetic parameters used for the relative rates of termination and propagation of radicals within the corresponding calculations. In doing so, we will go back to the interpretation of Figure 1 for a moment: The limiting situation, where $i_T$ is to be extracted from inflection points and which was calculated using "low" values of the start concentration of radicals, may be described more precisely as a situation in which the radical concentration half-value life $1/k_t c_R^{\max}$ during one pulse period[8] (which was approximately 0.06 s in this case) is comparable to the pulse period $T$ (which was 0.1 s for all calculations within the present investigation); i.e., loosely speaking, during the time required for their termination radicals may grow by the order of $i_T$ in length. It might be noted in passing that Figures 2 and 3 nicely illustrate the mature of *inflection points* at $i_T$: The *steepest ascents in $w(i)$* occur for the *steepest descents in $w_R(i,\tau)$*. The inflection points in $w(i)$ refer to those growing radicals which are subject to the highest termination rates and whose change in weight fraction with respect to their chain length is thus the largest. The instants of highest termination rates are determined by the entrance of a laser pulse. In the frame of eq 3 all radical chains which have not been terminated in the instant when a subsequent laser pulse enters the reaction volume have chain lengths of $i_T$ or of integral multiples thereof.

The second limit, where $i_T$ should better be extracted from the CLDs maximum and which was calculated using "high" values of the start concentration of radicals, may accordingly be described as a situation in which the radical concentration half-value life $1/k_t c_R^{\max}$ (which was 0.0009 s in that case) is very much shorter than the pulse period $T$ of 0.1 s which means that, during the time required for their termination, radicals may only grow by a corresponding small fraction of $i_T$ in length. In other words, just to emphasize these important findings, it is suggested that $i_T$ be extracted from low molecular weight side inflection points or from maxima of PIO structures within CLDs of PIO polymer, when the pulse period $T$ is *"very much longer"* or *"of the order of or shorter"* than the radical concentration half-value life $1/k_t c_R^{\max}$, respectively. The former and the latter limiting experimental situations of the PLP technique will hereafter be referred to as the *low* and the *high termination rate limits*, respectively.

Provided $Tk_t$ is of the order of $10^7$ L mol$^{-1}$, the difference between $c_{R,0}^0$ and $c_R^{\max}$ is almost negligible at a level of $c_{R,0}^0 = 10^{-5}$ mol L$^{-1}$, so that hardly any radicals can survive more than 1 initiating pulse. Thus, in Figure 5, which was calculated with $c_{R,0}^0 = 10^{-5}$ mol L$^{-1}$ and 100% termination by disproportionation, the weight fraction of polymer as well as that of growing radicals with chain lengths above the (Poisson-broadened) value of $i_T$ is almost zero. Obviously, beyond some high value of the termination rate, the weight fraction of polymer with chain lengths above the (Poisson-broadened) value of $i_T$ may only be really significant in the case of combination-dominated termination (Figure 4). This is another important result of the present model calculations, because it would appear to permit an easy experimental test of whether termination is dominated by disproportionation or by combination, if it turned out to be real.

From the middle section of Figure 4 it becomes immediately clear why a minimum but not a maximum develops at $2i_T$ in the $\mathrm{d}w(i)/\mathrm{d}i$ curves of Figure 1 for the calculation using $c_{R,0}^0 = 10^{-5}$ mol L$^{-1}$, together with termination being predominantly in the combination mode. This minimum does not indicate the chain length which corresponds to radical chains that have grown over the period of $2T$ (as maxima in d$w(i)$/d$i$, or in $w(i)$, are supposed to do within the present understanding of PLP kinetics) but the chain length which indicates the limit up to which polymer may be formed when radicals grow over time $T$ and when termination is by combination. Of course, these two chain lengths, i.e. that of a radical which grew over $2T$ and that of polymer combined out of two radicals which grew over $T$, should ideally be identical. The slight underestimation of $2i_T$ by the minimum in the d$w(i)$/d$i$ curve obtained for $c^0_{\mathrm{R},0} = 10^{-5}$ mol L$^{-1}$ results from termination being partly in the disproportionation mode. A look at the inserts in the middle and lower sections of Figure 5, where the distributions $\Delta w(i,T)$ and $w_\mathrm{R}(i,T)$, respectively, have been replotted on an expanded scale, reveals that finding a minimum in d$w(i)$/d$i$ at $2i_T$, i.e. an inflection point at the high molecular weight side of CLDs of PIO polymer, is obviously a special feature of systems in which high values of start concentrations of radicals are used and in which termination is by combination, because if termination is by disproportionation in such systems, the value of $2i_T$ coincides with a maximum of the corresponding CLD. The distributions of weight fractions of growing radical chains in Figures 4 and 5 are again identical, irrespective of the mode of termination.

## Experimental Section

For the purpose of experimental verification of the model calculations obtained on the basis of eq 3 so far, pulsed laser polymerizations were performed with styrene (S) and methyl methacrylate (MMA) at 25 °C. CLDs of the resulting polymer material were measured by SEC.

Monomers were destabilized by washing with dilute alkali and subsequently passed through a column filled with activated alumina (Aluminum oxide 90, Merck). 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Aldrich) was used as photoinitiator in concentrations of around 5 mmol L$^{-1}$ as received. A pulsed excimer laser (RD-EXC-150, Radiant dyes) was operated at 308 nm (XeCl) and used together with a dye laser (Radiant dyes) to produce light pulses at 355 nm. The pulse width was approximately 20 ns. Pulse periods were set to 0.1s for all experiments. The reactions were carried out in quartz tubes which, after purging with He, were sealed with quartz windows. The quartz tubes were thermostated at 25 ± 0.2 °C. Directly after laser irradiation, the monomer samples were diluted with excess dichloromethane (Lichrosolv, Merck), which contained a small amount of 2,2,6,6-tetramethylpiperidin-1-oxyl free radical (TEMPO, Janssen Chimica) as inhibitor.

When the CLDs of the polymers formed during PLP were analyzed by means of SEC, the monomer conversions were simultaneously controlled to ensure that they were always below 1% via a calibrated differential refractometer (RI 71, Merck) signals. Five columns (Ultrastyragel, 500, $10^3$, $10^4$, $10^5$, and $10^6$ Å, Waters) were used as 25 °C. The eluent was dichloromethane (Lichrosolv, Merck) with a flow rate of 1 mL min$^{-1}$. Calibrations were performed with polystyrene (PS) or poly(methyl methacrylate) (PMMA) standards, which had narrow CLDs and precisely known molecular weights (Polymer Standard Service).

For the purpose of large experimental variations of the radical concentration half-value lives, it appeared most suitable to vary the energy of initiating laser pulses, while it is understood that this goal should in principle be also attainable to some extent by varying, e.g., the viscosity of the reaction system and thereby $k_\mathrm{t}$, or by varying the initiator concentration, the initiator itself, or the laser wavelength. Laser pulse energies were varied by widening the laser beam diameter using a quartz lens. Actual energies per area of illuminated monomer surface were measured through suitable apertures by averaging over 100 single pulses using a pyrometric energy detector (PRJ-M, Gentec). Absorptions of the reaction mixtures were controlled by UV spectroscopy to be of the order of 0.5 for monomer layers of about 1 cm thickness at 355 nm prior to laser exposure. No attempt was made to ensure homogeneous illumination of the reaction volume. This rough experimental design was assumed to be sufficient for the present purpose. It was assumed that laser pulses of different diameters defined their own reaction volume anyway, irrespective of what fraction of the whole sample was actually illuminated. We may really assume that even if a small fraction of radicals produced per laser pulse would in fact diffuse out of the illuminated reaction volume within one pulse period—and as a consequence would not be subjected to termination at such a high rate as in the illuminated volume—this would not change the essence of our proposal to determine $k_\mathrm{p}$ from the maxima of CLDs when high termination rates are being used.

PLPs with high-energy pulses tend to give rise to an increased amount of oligomeric species. With special respect to the determination of the weight fraction of the oligomers formed, samples were directly injected into the SEC apparatus rather than after prior precipitation and separation of the polymer. An eventual drift of the SEC retention times due to flushing of the columns with large amounts of unreacted monomer was checked for by comparison with SEC traces from precipitated, i.e. monomer-free, polymer samples. For the present purpose, this procedure was preferred because it is even more simple than the evaporation of excess monomer, which may be another route to correct the measurement of oligomer contents.

## Results

Experimental results for CLDs $w(i)$ of polymer from PLPs of styrene and methyl methacrylate at 25 °C in bulk together with corresponding numerically obtained derivatives d$w(i)$/d$i$ are plotted against polymer chain length $i$ in Figures 6 and 7, respectively. The pulse period was exactly set to $T = 0.1$ s in all cases. Laser pulse energies per area of illuminated monomer surface were roughly 0.02 mJ cm$^{-2}$ (fine broken curves), 0.2 mJ cm$^{-2}$ (bold broken curves), 2 mJ cm$^{-2}$ (fine full curves), and 20 mJ cm$^{-2}$ (bold full curves). Dotted vertical lines have been drawn into Figures 6 and 7 at $i_T = j80$ with $j = 1-4$ and at $i_T = j335$ with $j = 1-3$, respectively, as "best estimates" of inflection points of PIO *shoulders* measured for the lowest laser pulse energies. By doing so, the general trend suggested by the calculations shown in Figure 1 appears to be well reflected by these experiments; i.e. the maximum chain lengths of PIO peaks approach these estimates as they evolve from the CLD due to an increased energy (or start concentration of radicals) per initiating laser pulse, while the low molecular weight inflection points of $w(i)$, i.e. the maxima within d$w(i)$/d$i$, move away more and more from these estimates at the same time. According to the chain lengths corresponding to the dotted vertical lines in Figures 6 and 7, propagation rate coefficients of $k_\mathrm{p}$(S, 25 °C) = 92 L mol$^{-1}$ s$^{-1}$ and $k_\mathrm{p}$(MMA, 25 °C) = 359 L mol$^{-1}$ s$^{-1}$ were determined for the free-radical bulk polymerization of styrene and methyl methacrylate, at 25 °C, using monomer concentrations at this temperature[9] of $c_\mathrm{M}$(S, 25 °C) = 8.65 mol L$^{-1}$ and $c_\mathrm{M}$(MMA, 25 °C) = 9.34 mol L$^{-1}$. Olaj et al.[9] published significantly lower values of $k_\mathrm{p}$(S, 25 °C) = 77 L mol$^{-1}$ s$^{-1}$ and $k_\mathrm{p}$(MMA, 25 °C) = 313 L mol$^{-1}$ s$^{-1}$, which—irrespective of the actual radical concentrations half-value lives—were taken from inflection points within CLDs of PIO polymer. In view of the calculations shown in Figure 1, this significant underestimation is readily understood; i.e. only in the low termination rate limit will the characteristic inflection points of the low

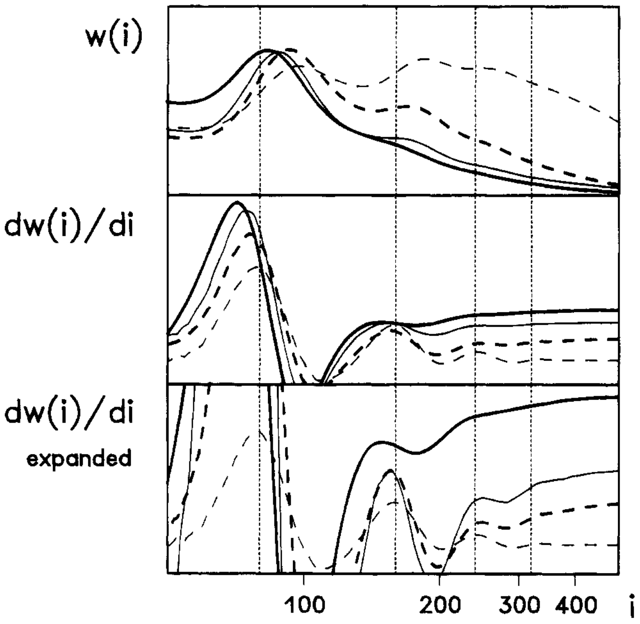

**Figure 6.** Experimental chain length distributions *w(i)* and numerically obtained derivatives d*w(i)*/d*i* thereof for a pulsed laser polymerization of bulk styrene at 25 °C. Laser pulse energies per area of illuminated monomer surface were roughly 0.02 mJ cm$^{-2}$ (fine broken curves), 0.2 mJ cm$^{-2}$ (bold broken curves), 2 mJ cm$^{-2}$ (fine full curves), and 20 mJ cm$^{-2}$ (bold full curves). Values of ordinates were plotted in arbitrary units against chain length *i*. Values of $i_T$ and integral multiples thereof are indicated as dotted vertical lines.

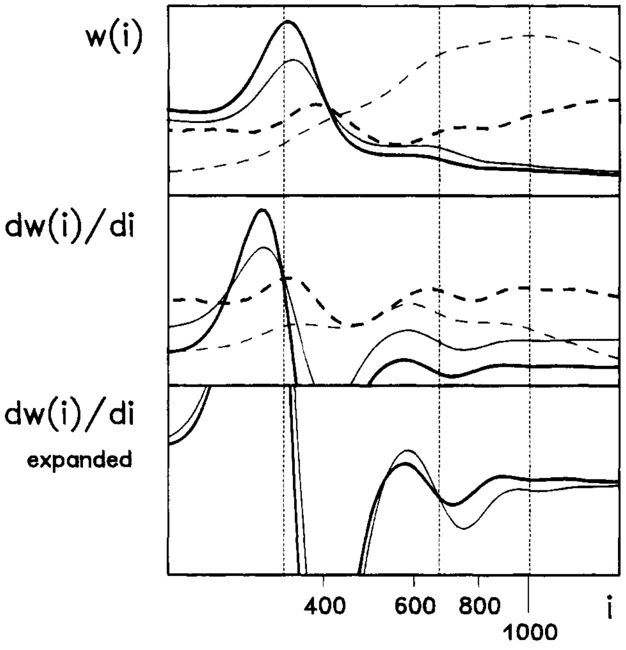

**Figure 7.** Experimental chain length distributions *w(i)* and numerically obtained derivatives d*w(i)*/d*i* thereof for a pulsed laser polymerization of bulk methyl methacrylate at 25 °C. Laser pulse energies per area of illuminated monomer surface were roughly 0.02 mJ cm$^{-2}$ (fine broken curves), 0.2 mJ cm$^{-2}$ (bold broken curves), 2 mJ cm$^{-2}$ (fine full curves), and 20 mJ cm$^{-2}$ (bold full curves). Values of ordinates were plotted in arbitrary units against chain length *i*. Values of $i_T$ and integral multiples thereof are indicated as dotted vertical lines.

molecular weight side of PIO structures be the correct measures of $i_T$. These inflection points may, however, be an underestimation, if the actual radical concentration half-value life is significantly shorter than is required in this limit.

Due to limited energies per laser pulse, the high termination rate limit is not entirely attained, in either Figure 6 or 7. Surprisingly, not only for the case of S, where predominant termination by combination is generally assumed, but also for the case of MMA, where the extent of approach to the high termination limit appears to be even higher as compared to S, does the CLD obtained for the maximum laser pulse energy suggest that termination is predominantly of the combination type. Evidence for this suggestion not only comes from the character of *w(i)* but may also be seen in the approach of the minimum in d*w(i)*/d*i* toward $2i_T$ (compare considerations above). This observation is especially interesting, because termination within free-radical polymerizations of MMA is normally assumed to be predominantly of the disproportionation type (see for instance refs 10 and 11).

Some further peculiarities emerge from Figures 6 and 7. The derivative d*w(i)*/d(*i*) obtained for the PLP of styrene shows well-defined and in this sense reliable maxima even at the lowest energy per pulse, while this is not so clear within the corresponding curves obtained for the polymerization of MMA. It is estimated that this result is due to indistinct PIO structures and correspondingly large experimental error. On the other hand, in the experiment with the highest laser power density and in particular with the PLP of styrene, where the laser light defined only a comparatively small reaction volume, a significant amount of radicals obviously escaped termination by successive laser pulses and, as a consequence, were able to reach high molecular weights.

It has been discussed above that pulsed-laser initiation originating structures tend to diminish, when progressing from high to low values of initiating pulse energies (or start concentrations of radicals or termination rates). Model calculation using eqs 3 and 4 already revealed (compare, e.g., Figure 1) that one kinetic origin of this tendency may be the process of radical growth parallel to termination, the appearance of which increases the more the radical concentration half-value lives are prolonged. Ultimately, this trend will lead to untypically smooth, i.e. unstructured CLDs, which completely hinder the determination of inflection points characteristic for $k_p$. Just to distinguish it from the "low termination rate limit", such a situation might be called "the high propagation rate limit". This notation would emphasize that radicals are able to grow by many times of $i_T$ in length during the time of their termination in this limit.

It is interesting to note in this context that the PLP method has been hampered when applied to rapidly polymerizing monomers in bulk, like acrylates for instance, and, very recently, to vinyl acetate (see for instance ref 12 and references cited therein). The method was not working with these monomer systems, simply because no PIO structures could be obtained. In attempts to unravel the kinetic reasons behind this fully substantiated experimental observation, transfer reactions to monomer, for instance, have been discussed. These reactions are supposed to have some effect toward making PIO structures indistinct, inasmuch as they diminish the concentration of radicals having well-defined lifetimes of integral multiples of the pulse period. As a result of mathematical modeling, it was however already suggested that consideration of transfer rate coefficients usually involved in those systems may perhaps not account solely for the observed unstructured CLDs.[12] Such a conclusion may essentially also be derived from a closed form solution of the CLD for instantaneously initiated free-radical polymerizations of Yan et al.,[13] which allows for a calculation of the distribution of growing polymer chains after a single initiating pulse accounting for transfer to monomer. It has been recently observed, but not yet understood, that making the concentration of monomer small or choosing low temperatures, i.e. essentially making the rate of radical propagation small, resulted in the development of very clearly observed PIO structures.[12,14] In view of the interpretation of eq 3 given so far, one physical reason for such ways of arriving at structured CLDs might be a departure from what has just been called the high propagation rate limit. Provided all other experimental parameters like, for instance, the energy and the repetition rate of laser pulses, the rate of transfer reactions to monomer or solvent, and the CLDs resolution remained unchanged, those "evolutions of PIO structures" would then be said to result from a corresponding decrease of some effective radical concentration half-value life. Consideration of "effective termination rates" might be rationalized by introducing local radical concentrations or by assuming active ends of radicals being shielded from termination within their own large chains.[15] Such effects, which might effectively mean considering radical chain-length-dependent termination, would increase with increasing chain length, i.e. if radicals can grow to large chain lengths during $T$ in high-$k_p$ systems, the lowering of the termination rates due to "homogeneously compartmentalized" radicals could result in correspondingly diminished PIO structures or, ultimately, in arriving at the high propagation limit.

Although the situation of obtaining CLDs apparently without any PIO structures is definitively contained in eq 3,[16] the value of corresponding parameter variations, which aim at an estimation of the degree of an approach to the high propagation limit, is questionable, because essential sources of broadening the observed structures like radical chain transfer reactions and, perhaps more importantly, instrumental broadening are not contained in (3).

A comparison of the experimental CLD of Figure 7 obtained at the highest energy per laser pulse for MMA at 25 °C with a calculation according to eq 3 using $k_p = 359$ L mol$^{-1}$ s$^{-1}$, $c_M^N = 9.34$ mol L$^{-1}$, $T = 0.1$ s, $k_{tc} = 10^8$ L mol$^{-1}$ s$^{-1}$, $k_{td} = 0$ L mol$^{-1}$ s$^{-1}$, and $c_{R,0}^0 = 10^{-5}$ mol L$^{-1}$ is shown in Figure 8. Chain transfer to monomer is assumed to be negligible under the conditions of this experiment.[17] It is therefore further assumed that the calculated width of the PIO peak around $i_T$ at 335 is equal to the minimum theoretically possible for MMA radical chains, that have grown to this length by radical polymerization. As compared with the calculated CLD, the approach of the chain length at the maximum of $w(i)$ near $i_T$ to 335 as well as the approach of the chain length at the minimum of d$w(i)$/d$i$ near $2i_T$ to 770 is less marked within the experimental CLD. Nevertheless, the chain length at the low molecular weight side inflection point of the experimental CLD, which is approximately 300 according to the chain length at the maximum in d$w(i)$/d$i$ in the middle section of Figure 8, underestimates the corresponding value of the calculated CLD by about 7% and the calculations input of $i_T = 335$ (which was chosen to be equal to the value of its best estimate within Figure 7) by about 11%. Thus, if experimental broadening occurs, an underestimation of $i_T$ appears to be inevitable, if it is derived from low molecular weight inflection points of experimental PIO structures. Also the overestimation of $2i_T$ by the minimum of d$w(i)$/d$i$ in the lower section of Figure 8 might to some extent result from experimental broadening. If the excess width of the experimental peak (as compared to the width of the calculated one) may be attributed to experimental broadening, an underestimation of $i_T$ resulting solely from this kind of experimental error of the order of 5% may be estimated from Figure 8. In chromatographically more unfavorable situations this error might as well be significantly larger. On the other hand, the influence of broadening on $i_T$ is assumed to be much more readily restrictable if an experimental situation prevails, where it is to be taken from maxima of PIO peaks.

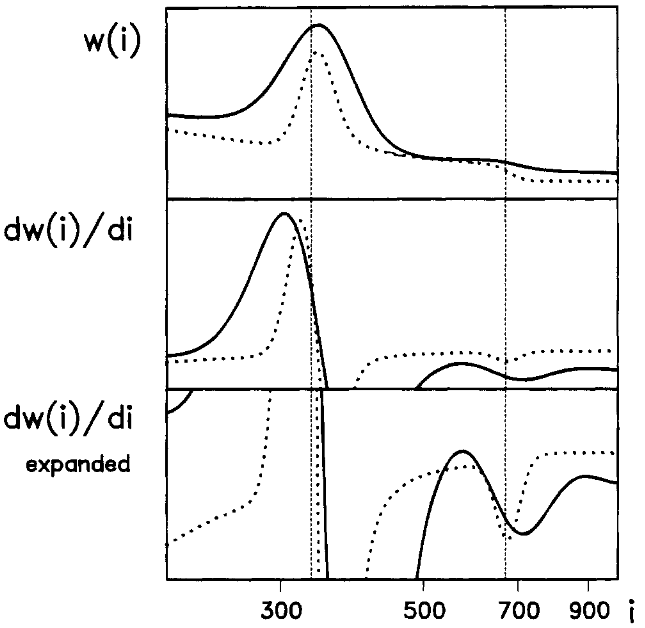

**Figure 8.** Comparison of experimental (full curves) and calculated (dotted curves) chain length distributions $w(i)$ and numerically obtained derivatives d$w(i)$/d$i$ thereof for a pulsed laser polymerization of bulk methyl methacrylate at 25 °C. Experimental parameters correspond to the 20 mJ cm$^{-2}$ experiment of Figure 7, while the parameters used within eq 3 were $k_p = 359$ L mol$^{-1}$ s$^{-1}$, $c_M^N$ = constant = 9.34 mol L$^{-1}$, $T = 0.1$ s, $k_{tc} = 10^8$ L mol$^{-1}$ s$^{-1}$, $k_{td} = 0$ L mol$^{-1}$ s$^{-1}$, $c_{R,0}^0 = 10^{-5}$ mol L$^{-1}$, and Int$(t/T) = n^* = 2$; values of ordinates were plotted in arbitrary units against chain length $i$. Values of $i_T$ and integral multiples thereof are indicated as dotted vertical lines.

## Conclusions

Obviously, some of the essential kinetic peculiarities of pulse-periodic initiation applied to free-radical polymerization in homogeneous systems are accounted for in eq 3.[5,6,18,19] It is to be noted that, although Aleksandrov et al. did not explicitly hint at the possibility of using the PLP approach to obtain absolute values (let alone make a suggestion of when to use the inflection points or the maxima as the preferred measure) of $k_p$, the fact that PIO peaks appear in close proximity to calculation inputs of multiples of $i_T$ was already evident from a model calculation by these authors.[3]

Having differences of the order of 10%−20% in mind, which are usually to be considered with respect to the extent of experimental agreement of chain lengths at low molecular weight side inflection points and maxima of PIO structures, the present investigation may perhaps be understood as a small contribution to the refinement of the yet unparalleled PLP technique[2] for measuring $k_p$. This refinement is, however, worthwhile with respect to an optimized precision as well as with regard to the ultimately attainable accuracy of the method. In this sense it appears to be essential in efforts to obtain benchmark values of kinetic rate parameters in free-radical polymerization systems[1,20] or in examinations of tiny solvent effects on $k_p$ (see, e.g., refs 9 and 21).

For experimental practice, it would be helpful to have some guidelines for deciding when to use inflection points or maxima for the determination of $k_p$, because, usually, we will not have any precise a priori knowledge for instance of the relevant radical concentration half-value life for the system under consideration, and even if we had, i.e. if we knew the produced start concentrations of radicals per laser pulse and had a reliable mean termination rate coefficient at hand, we would still be left alone without knowing reliably the dependence of the termination rate on radical chain lengths. This means that we should be aware of the possibility that the termination reaction which takes place between radicals of chain length $ji_T$ ($j$ = 1, 2, 3, ...) and instantaneously produces very short radicals might be very much more rapid than termination reactions on the basis of mean termination rate coefficients suggest. In view of the present investigation, such problems seem to be circumventable by simple visual inspection of experimental CLDs: In the high termination rate limit, where clearly resolved PIO peaks occur in the CLD which do not shift to lower chain lengths due to a further increase of the start concentration of radicals and which decrease rapidly in weight fraction as the chain length increases, the best measure of $i_T$ should be maxima of these peaks. In the low termination rate limit, where only shoulders are to be seen in experimental CLDs and where, within the first few shoulders, the weight fraction of polymer increases from shoulder to shoulder, the best measure of $i_T$ should be the low molecular weight side inflection points of these shoulders, if they do not shift toward larger chain lengths when the start concentration of radicals is further decreased. Experimental CLDs between these two limits may result in slight over- or underestimations of $k_p$, when it is deduced from maxima or low molecular weight side inflection points of PIO structures, respectively.

One final suggestion should be made with respect to the benefits which CLD analyses of polymer produced by pulsed initiation using high values of start concentrations of radicals may have, as compared to experiments with low start concentrations. Beyond unique information on the mode of termination which such experiments are supposed to yield and beyond the lower sensitivity of maxima (as compared to inflection points) to errors resulting from peak broadening, the use of matrix-assisted laser desorption/ionization mass spectrometry (MALDI) might be the obvious choice for the analysis of the CLDs of the produced polymer material for two reasons: Firstly, in PLPs with high start concentrations of radicals the production of low molecular weight material is favored, which is also the preferred range of MALDI application. Secondly, peak maxima appear to be more precisely locatable as compared to inflection points, especially as far as MALDI is concerned.[22] The successful combination of PLP and mass spectrometry would not only remove the difficulty of obtaining absolute molecular weight distributions for unknown copolymers or even multipolymers, which has been one of the major drawbacks of the PLP/SEC approach up to now, but would at the same time also significantly increase the precision and accuracy of free-radical polymerization propagation rate coefficients so obtained.

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(7) $n^*$ may be determined using simple numerical simulations of the approach of the numerically determined total concentration of radicals at $\tau' = 0$ to $c_R^{max}$ in the course of the first few initiating pulses.

(8) In the context of pulse-periodic initiation, the concept of looking at the radical concentration half-value lives is especially illustrative if lifetimes shorter than $T$ are looked at, because only then can the radical concentration half-value life be expressed simply by $1/k_t c_R^{max}$.

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(16) These calculations will however tell us that taking the low molecular weight inflection points of unstructured experimental CLDs as a *lower* limit of $i_T$, may theoretically very well be an overestimation (compare for instance: Davis, T. P.; O'Driscoll, K. F.; Pitton, M. C.; Winnik, M. A. *Polym. Int.* **1991**, *24*, 65).

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(18) An easy extension of eq 3 to account for instance for radical chain length dependent termination reactions or for transfer reactions does not seem to be within close reach. The consideration of such complicating, although really common, features of free-radical polymerization systems appears to be reserved to Monte Carlo techniques of calculation. Compared with the deterministic closed form solution of Aleksandrov et al.,[3] such stochastic approaches toward simulation of CLDs of pulsed-laser-made polymer suffer however from the calculation time needed and/or from the limited molecular weight range up to which calculations may be performed within reasonable times.

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