New Aspects of Chain-Length Dependent Termination

Oskar Friedrich Olaj, Andreas Kornherr, Philipp Vana, Monika Zoder, Gerhard Zifferer*

Institut für Physikalische Chemie, Universität Wien, Währinger Straße 42, A-1090, Austria

Summary: A survey is given on a selection of recently developed methods for the evaluation of the rate coefficient k_t of termination and its chain-length dependence. In particular these are the time-resolved single-pulse pulsed laser polymerization (TR-SP-PLP), the single pulse pulsed laser polymerization in combination with the analysis of the molecular weight distribution produced (SP-PLP-MWD), the methods yielding an average k_t either from the second moment of the chain-length distribution (CLD) or from the rate of polymerization, and a method focusing on the chain-length dependence of k_t consisting in an analysis of the CLD resulting from PLP experiments carried out at low pulse frequencies (LF-PLP). The results obtained by these methods are compared and discussed. The role of the shielding of the two radical chains by their appendant coils is emphasized.

Introduction

Compared to the other elementary steps in radical polymerization the termination process certainly is the most complex one. While propagation – at least under normal initial conditions – is a comparatively simple activation-controlled reaction between a radical chain and a neutral monomer molecule again leading to a radical chain whose length is increased by one monomer unit, termination consists of a complicated sequence of steps (approach of the two radical chains by center of mass diffusion, mutual interpenetration of the coiled radicals, translational and rotational diffusion of the radical chain ends, final spin annihilation) all mostly physical in nature. Contrary to some other examples in reaction kinetics where physical processes can be described with much more ease than chemical ones this is not so with the termination reaction between two polymer radicals, mainly because of the complex "entanglement" of the part steps named above. One of the main consequences is also that at least some of these part steps should be chain-length dependent, calling for a chain-length dependence of the termination rate constant k_t as a whole, too. In this case two additional problems arise: (a) because there is a genuine polydispersity of living chains in all polymerization systems k_t has to be assigned (and refers) to this chain-length distribution (CLD) to be characterized at least by its mean chain length, and (b) due to the *bimolecular* nature of

© WILEY-VCH Verlag GmbH, 69469 Weinheim, 2002 CCC 1022-1360/00/$ 17.50+.50/0

the termination process k_t accordingly will depend on some average ($\overline{i, j}$) of the lengths of the two chains (i, j) involved. Both these facts imply that k_t cannot have the meaning of a *kinetic constant* but has to be treated as a *kinetic coefficient* rather.

This is considered as *one* of the main reasons why our knowledge of k_t values is much less developed than that pertaining to the other elementary constants of radical polymerization. The *second* point is caused by the fact that no methods were available in the past which aimed at a *direct* determination of k_t; in fact k_t always appeared as some aggregate with the propagation constant k_p. For decades the only access to k_t data was to combine k_p^2/k_t values (to some power n) from *stationary* free radical polymerizations with k_p/k_t values from experiments carried out under *nonstationary* or *pseudostationary* conditions and to resolve these ratios into their individual components k_p and k_t. Not only that this involves a lot of problems if – as it is nearly always the case – the two types of experiments refer to basically different radical chain-length distributions, this indirect manner of determining the two quantities k_p and k_t is overloaded with such an extent of inaccuracy that no reliable solutions to these two equations for the two unknowns, k_p and k_t, can be obtained.[1] A short look into the Polymer Handbook[2] of 1989 conveys an impressive picture of the situation: the k_t data are scattered over about 1.5 decades even for the two well-behaved and best-investigated monomers styrene (St) and methyl methacrylate (MMA). Relying on the latest edition (1999) of the Polymer Handbook[3] little or nothing seems to have changed in the meantime. Actually, the situation may not be seen in such a pessimistic way. Without making any claim for completeness it is the primary intention of this article to give some account of

a) The methods for the assessment of k_t that have been developed since 1989

b) The results obtained

New Methods

Progress in determining k_t to some extent was more or less automatically announced by the experimental realization[4,5] of the so-called PLP (pulsed laser polymerization) method in 1987 which allows a *direct* determination of k_p from the analysis of the CLD of (dead) polymer prepared by periodic pulsed laser initiation. When t_0 is suitably chosen the CLD exhibits inflection points $(L_0)_n$ on the low molecular weight side of its "extra peaks" which fairly well obey the relationship

$$(L_0)_n = n \cdot t_0 \cdot k_p \cdot [M] \qquad (1)$$

t_0 = time elapsing between two successive pulses

[M] = monomer concentration

where n characterizes the "order" of the point of inflection. As a matter of fact, this technique has developed into a standard and benchmark method during the fourteen years of its existence and has provided k_p data for a lot of monomers, e.g. styrene, methyl methacrylate, a series of acrylates and other methacrylates, vinyl acetate etc.[6-9] Not unexpectedly, a lot of the problems[1] which are associated with the *indirect* determination of k_t from two different combinations of k_p and k_t disappear when a directly determined k_p is used to resolve one of these combinations into their individual constituents. What is left in any case, however, is to find a convenient way to obtain reliable information not only on k_t but also on its chain-length dependence.

1) k_t *from the time-resolved decrease of monomer concentration following a single laser pulse (time-resolved single-pulse pulsed laser polymerization, TR-SP-PLP)*

This method applies the ingenious technique originally developed by Buback *et al.*[10,11] which consists in the time-resolved registration of the (decrease of) monomer concentration following a laser pulse. In the form described below[12] it follows a (theoretical) paper by de Kock *et al.*[13] Solving the equation for the (instantaneous) rate of polymerization $\upsilon_p(t) \equiv -\mathrm{d[M]}_t/\mathrm{d}t$ for the (instantaneous) radical concentration $[\mathrm{R}\cdot]_t$

$$[\mathrm{R}\cdot]_t = \frac{1}{k_p[\mathrm{M}]}(-\mathrm{d[M]}/\mathrm{d}t) \tag{2}$$

and simultaneously solving the equation defining the rate of termination υ_t

$$-\frac{\mathrm{d}[\mathrm{R}\cdot]_t}{\mathrm{d}t} = k_t[\mathrm{R}\cdot]_t^2 \tag{3}$$

for k_t, whether this be a constant or a properly averaged rate coefficient of termination

$$k_t = \frac{1}{[\mathrm{R}\cdot]_t^2}(-\mathrm{d}[\mathrm{R}\cdot]_t/\mathrm{d}t) \tag{4}$$

a combination of Eqs.(2) and (4) leads to[13]

$$k_t = k_p\left[\frac{[\mathrm{M}]_t\cdot[\ddot{\mathrm{M}}]_t}{[\dot{\mathrm{M}}]_t^2} - 1\right] \tag{5}$$

where $[\dot{\mathrm{M}}]_t$ and $[\ddot{\mathrm{M}}]_t$ are the first and the second time derivative of the instantaneous monomer concentration $[\mathrm{M}]_t$ respectively.

If the laser pulse is considered to provide a δ pulse of initiation on the time scale of the experiment (i.e. all living chains are produced simultaneously) and accordingly have the same (time-dependent) chain-length within the small polydispersity of a Poisson-distribution k_t can be assigned with good accuracy to a certain chain-length i of the two

terminating chains on a microscopic scale which is related to time t after pulse initiation by an equation analogous to Eq.(1)

$$i = k_p \cdot [M] \cdot t \tag{1a}$$

provided k_p is chain-length independent, no radicals from former pulses are left in the system and chain transfer can be ignored

$$k_t^{i,i} = k_p \left[\frac{[M]_t \cdot [\ddot{M}]_t}{[\dot{M}]_t^2} - 1 \right] \tag{5a}$$

Of course, this treatment yields correct results only if no inhibitor is present in the system and if the initia[14]tor used is ideal. Prospects of successfully applying this method are best with monomers distinguished by high k_p values that accordingly give comparatively large conversions per pulse. The necessary condition, of course, is that the method of monitoring the disappearance of monomer following a laser pulse is sensitive enough to yield data of sufficiently high quality so that the second derivative of [M] is available with the necessary accuracy. What is left is the determination of $k_t^{i,j}$ rate coefficient of termination between radicals of different size. In principle, this could be done by an extension of TR-SP-PLP called TR-echo-PLP. Here a second laser pulse is applied shortly after the first one so that the problem of termination within an overall radical population is mainly reduced to termination between radicals of equal length produced in pulse nr.1 (governed by $k_t^{i,i}$) and nr.2 ($k_t^{j,j}$) and termination between radicals produced in pulse nr.1 and those in pulse nr.2 ($k_t^{i,j}$). From the latter the desired information on $k_t^{i,j}$ can be extracted.[12,15]

2) k_t *from the molecular weight distribution of single pulse experiments (SP-PLP-MWD; de Kock*[12]*)*

The crucial problem of the former method, the accurate evaluation of [M] can be circumvented by resorting to the CLD of the polymer formed in the single pulse experiment. Assuming for example termination by combination (no necessary condition) which means one polymer molecule of twice the length is formed from two radicals) the decrease in radical concentration can be replaced by the rate of polymer formation $d[P]_t/dt$

$$\frac{d[P]_t}{dt} = -\frac{1}{2}\frac{d[R\cdot]_t}{dt} \tag{6}$$

Accordingly $[R\cdot]_t$ can be written as

$$[\mathrm{R}\cdot]_t = [\mathrm{R}\cdot]_0 + \int_0^t \frac{\mathrm{d}[\mathrm{R}\cdot]_t}{\mathrm{d}t}\mathrm{d}t = [\mathrm{R}\cdot]_0 - 2\int_0^t \frac{\mathrm{d}[\mathrm{P}]_t}{\mathrm{d}t}\mathrm{d}t \tag{7}$$

Insertion of Eqs.(6) and (7) into Eq.(4) yields

$$k_t = \frac{2(\mathrm{d}[\mathrm{P}]_t/\mathrm{d}t)}{\left([\mathrm{R}\cdot]_0 - 2\int_0^t \frac{\mathrm{d}[\mathrm{P}]_t}{\mathrm{d}t}\mathrm{d}t\right)^2} \tag{8}$$

Using Eq.(1a) the time dependence in Eq.(6) again can be transformed into a chain-length dependence

$$\frac{\mathrm{d}[\mathrm{P}]_t}{\mathrm{d}t} = \frac{1}{V}\frac{\mathrm{d}N_{\mathrm{P},t}}{\mathrm{d}t} = \frac{2k_\mathrm{p}[\mathrm{M}]}{V}\frac{\mathrm{d}N_{2i}}{\mathrm{d}(2i)} \tag{9}$$

where $[\mathrm{P}]_t$ has been expressed as the amount of polymer molecules N_P in an (arbitrary) volume V. The derivative $\mathrm{d}N_{2i}/\mathrm{d}(2i)$ of course is the (differential) number distribution n_{2i} (the unusual form being a consequence of the choice of the termination mode). Combining Eqs.(8) and (9) yields

$$k_\mathrm{t}^{i,i} = \frac{4k_\mathrm{p}[\mathrm{M}]n_{2i}}{V\left([\mathrm{R}\cdot]_0 - 2\int_0^i \frac{1}{V}n_{2i}\mathrm{d}i\right)^2} \tag{10}$$

Expressing the initial radical concentration $[\mathrm{R}\cdot]_0$ as double the number of polymer molecules formed per pulse

$$[\mathrm{R}\cdot]_0 = 2\int_0^\infty \frac{\mathrm{d}[\mathrm{P}]_t}{\mathrm{d}t}\mathrm{d}t = \frac{2}{V}\int_0^\infty n_{2i}\mathrm{d}i \tag{11}$$

Eq.(10) takes the form

$$k_\mathrm{t}^{i,i} = \frac{Vk_\mathrm{p}[\mathrm{M}]n_{2i}}{\left(\int_0^\infty n_{2i}\mathrm{d}i - \int_0^i n_{2i}\mathrm{d}i\right)^2} = \frac{Vk_\mathrm{p}[\mathrm{M}]n_{2i}}{\left(\int_i^\infty n_{2i}\mathrm{d}i\right)^2} \tag{12}$$

There are two “uncertainties” in this development which prevent a direct application of Eqs.(10) or (12). The first one is the quantity V which plays the role of a scaling factor, the second refers to the fact that the integration of n_{2i} cannot be really carried to infinity in practice, on the one hand because the effect of chain transfer can no longer be neglected in the high molecular weight region, on the other because the range of CLD determination is limited by the size exclusion limit of the analytical method (GPC) applied for the evaluation of the CLD. This means that some “truncation chain-length“ i_max has to be introduced which corresponds to a certain “residual“ radical concentration

$[\mathrm{R}\cdot]_{\mathrm{res}}$ present at the moment at which integration is stopped. The calibration problem as a whole might be solved by assessing values for $[\mathrm{R}\cdot]_0$ as well as for $[\mathrm{R}\cdot]_{\mathrm{res}}$, where $[\mathrm{R}\cdot]_0$ and $[\mathrm{R}\cdot]_{\mathrm{res}}$ might be calculated via $k_{\mathrm{t}}^{1,1}$ from the Smoluchowski equation (or taken from literature data if available) in combination with $\overline{k_{\mathrm{t}}}$ data linking $[\mathrm{R}\cdot]_0$ and $[\mathrm{R}\cdot]_{\mathrm{res}}$ or alternatively from TR-SP-PLP traces.

3a) $\overline{k_{\mathrm{t}}}$ *from the second moment of the CLD (i.e. from PLP rate and* $\overline{P}_{\mathrm{w}}$ *data)* $\Rightarrow \overline{k_{\mathrm{t}}^{\mathrm{m}}}$

3b) $\overline{k_{\mathrm{t}}}$ *from PLP rate data alone* $\Rightarrow \overline{k_{\mathrm{t}}^{*}}$ *(Olaj et al.)*

Both methods are applicable at low conversions only.

In case of chain-length *in*dependent termination a surprisingly simple expression can be derived for pseudostationary polymerization[16] if chain transfer is negligible

$$\overline{P}_{\mathrm{w}} \cdot \upsilon_{\mathrm{p}} = \frac{k_{\mathrm{p}}^2}{k_{\mathrm{t}}}[\mathrm{M}]^2(3-\delta) \tag{13}$$

δ being the contribution of disproportionation to overall termination, $\overline{P}_{\mathrm{w}}$ representing the weight average degree of polymerization.

When applied to chain-length *dependent* termination Eq.(13) is still valid with k_{t} now representing an average ($\overline{k_{\mathrm{t}}^{\mathrm{m}}}$) shown to be a fair measure of the true *correctly* defined event-weighted average $\langle k_{\mathrm{t}} \rangle$ by simulation experiments[17]

$$\frac{\langle k_{\mathrm{t}} \rangle}{k_{\mathrm{t}}^{1,1}} = \frac{\int_0^{t_0} \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j}[\mathrm{R}_i\cdot][\mathrm{R}_j\cdot]\mathrm{d}t}{\int_0^{t_0} \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} [\mathrm{R}_i\cdot][\mathrm{R}_j\cdot]\mathrm{d}t} \tag{14}$$

Actually, the product $\upsilon_{\mathrm{p}} \cdot \overline{P}_{\mathrm{w}}$ represents the second moment of the CLD (per time) so that this method of determining k_{t} refers to a determination of this moment (symbolized by the index m in $\overline{k_{\mathrm{t}}^{\mathrm{m}}}$).

The characteristic equation for the rate in a PLP experiment with chain-length independent termination reads[18]

$$\upsilon_{\mathrm{p}} = \frac{1}{t_0}\frac{k_{\mathrm{p}}[\mathrm{M}]}{k_{\mathrm{t}}} \ln\left\{1+\frac{\rho\, k_{\mathrm{t}} t_0}{2}\left[1+\left(1+\frac{4}{\rho k_{\mathrm{t}} t_0}\right)^{1/2}\right]\right\} \tag{15}$$

where ρ has the same meaning as $[\mathrm{R}\cdot]_0$ before. Again this equation can be used to define

an average k_t in case of chain-length dependent termination, this time denoted as $\overline{k_t^*}$. By simulation it could be shown to be a nearly ideal representation of the correct average $\langle k_t \rangle$. It is common to $\overline{k_t^m}$ and $\overline{k_t^*}$ that – although $\overline{k_t^m}$ due to the different type of averaging is always about 15% smaller than $\overline{k_t^*}$ – simulations carried out with an input $k_t^{i,j}$ following a power law

$$k_t^{i,j} = k_t^{1,1} \cdot \left(\overline{i,j}\right)^{-b} \tag{16}$$

($\overline{i,j}$ being some properly defined average of chain-lengths i and j) always return an average $\overline{k_t}$, $\overline{k_t^m}$ or $\overline{k_t^*}$, which exhibits the correct exponent b with fair accuracy when plotted on a double logarithmic scale vs. ν' (the average length of all chains when undergoing termination)[17,19]

$$\overline{k_t^*}/k_t^{1,1} = A_{red}^{(*)} \cdot (\nu')^{-b} \tag{17a}$$

$$\overline{k_t^m}/k_t^{1,1} = A_{red}^{(m)} \cdot (\nu')^{-b} \tag{17b}$$

$A_{red}^{(*)}$ and $A_{red}^{(m)}$ being of the order of unity irrespective of whether type of averaging the two chain-lengths i and j of the two terminating living chains is used.[20]

Although $\overline{k_t^*}$ at the first glance seems to be insensitive toward the occurrence of chain transfer this is not the case in practice because not only ν' but also ρ have to be evaluated from the number average degree of polymerization $\overline{P}_n$ according to

$$\nu' = \frac{\overline{P}_n(1+\delta)}{2} \tag{18}$$

$$\rho = 2\upsilon_p t_0 / \left(\overline{P}_n(1+\delta)\right) \tag{19}$$

respectively, both equations being valid only for negligible chain transfer.

4) *Extent of chain-length dependence (characterized by exponent b) from the CLD of low frequency (LF)-PLP experiments (Olaj et al.*[21]*)*

This method resembles the SP-PLP-MWD method described before in as much as it is also based on the CLD of pseudo-SP experiments (more correctly these are LF-experiments rather than SP-experiments). Equal chain-lengths of the two reacting radicals is assumed here, too, and in addition $k_t^{i,i}$ is postulated to obey a power law

$$k_t^{i,i} = k_t^{1,1} \cdot i^{-b} \tag{16a}$$

Kinetic treatment leads to the normalized CLDs x_P^D and x_P^C for disproportionation

($\delta = 1$) and combination ($\delta = 0$), respectively

$$x_P^{\mathrm{D}} = \frac{k_t^{1,1}\rho}{\Theta} P^{-b}\left(1+\frac{k_t^{1,1}\rho}{(1-b)\Theta}P^{1-b}\right)^{-2} \tag{20a}$$

$$x_P^{\mathrm{C}} = \frac{k_t^{1,1}\rho}{4\Theta}\cdot\left(\frac{P}{2}\right)^{-b}\left(1+\frac{k_t^{1,1}\rho}{(1-b)\Theta}\left(\frac{P}{2}\right)^{1-b}\right)^{-2} \tag{20b}$$

where x_P^{C} is normalized to ½ and Θ is an abbreviation for k_p[M]. The overall (number) distribution for an arbitrary contribution of disproportionation δ is constructed from Eqs.(20a) and (20b) according to

$$x_P = \frac{2}{1+\delta}\left(\delta\, x_P^{\mathrm{D}} + (1-\delta)\, x_P^{\mathrm{C}}\right) \tag{21}$$

In its transformation to the experimental conditions of evaluating the CLD by GPC

$$w_{\log P} = aP^2\left\{\delta\frac{P^{-b}}{\left(1+c\left(\frac{1}{1-b}\right)P^{1-b}\right)^2} + \frac{1-\delta}{4}\frac{\left(\frac{P}{2}\right)^{-b}}{\left(1+c\left(\frac{1}{1-b}\right)\left(\frac{P}{2}\right)^{1-b}\right)^2}\right\}\frac{2}{1+\delta} \tag{21a}$$

this equation contains three adjustable parameters a, b, and c. b is the exponent to be determined, a and c are not strictly independent of each other but are connected by a normalization constant which in practice is not experimentally accessible for the same reasons as outlined for de Kock's procedure. a, b, c are obtained from a fit of the CLD to Eq.(21a). In most cases a constant set of parameters is obtained for a broad range of the CLD. Note that only exponent b but not k_t itself can be determined by this method. Although knowledge of k_p is not necessary for evaluating parameter b, k_p is hidden in parameters a and c, of course, and Eq.(1a) relating time and chain-length is presumed to hold.

Results

1) *TR-SP-PLP*

Unfortunately this most promising[12] method gives disappointing results with respect to the chain-length dependence of $k_t^{i,i}$ even if several hundreds of such experiments are superposed (Figure 1). Rates of radical disappearance $\mathrm{d}[\mathrm{R}\cdot]_t/\mathrm{d}t$ derived from these data points are (equally) spread over positive and negative values if a cubic spline procedure is applied to these co-added data of 285 independent experiments so that the desired goal of evaluating $k_t^{i,i}$ appears to be out of reach. Even fitting $[\mathrm{M}]_t$ to four (elaborate)

functions (which are working equally well at this level) and using these functions to produce the derivatives necessary for the evaluation of Eq.(5a) also gives an ambiguous result: One group of functions produces a monotonous decay of $k_t^{i,i}$ with i while the other – after an initial decrease – first passes through a minimum and afterwards through a maximum exhibiting a decline again at large chain-lengths.[12] The only thing that can be reliably done with these $[M]_t$ profiles (and has been already successfully performed in many cases by Buback et al.[10,11]) is to make a fit to the [M] vs. t curve based on a second order decay of $[R\cdot]$, governed by a (time-averaged) $\bar{k}_t$.

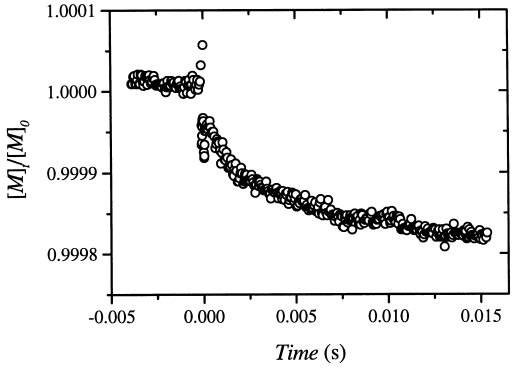

Figure 1. Relative monomer concentration $[M]/[M]_0$ vs. time for SP-PLP of methyl acrylate at 25°C. Data points accumulated from 285 experiments, for clarity only one tenth of the data points being shown.[12]

2) *SP-PLP-MWD*

Here the results largely depend on *how* the scaling of the CLD is performed.[12] If $k_t^{1,1}$ is calculated according to Smoluchowski and a cut-off chain-length of 2000 (corresponding to $[R\cdot]_{res}$) is chosen the experimental CLD can be transformed to k_t as a function of chain-length, the value of $k_t^{1,1}$ checked by extrapolation and the data re-scaled. The surprising result is that there are three different regimes (Figure 2, Table 1): Range A (i = 6–10), B (i = 15–30) and C (i = 50–100) in which definitely different exponents b are found when k_t is cast into the form of Eq.(16a), being 0.4–0.8 for range A, markedly higher in range B (1.1–1.2) finally taking moderate values (0.2–0.4), depending on the monomer (higher for methyl acrylate (MA) and ethyl acrylate (EA), lower for butyl acrylate (BA) at 25°C).

Table 1: Chain-length exponents b at 25°C over three different ranges of chain-lengths

Monomer	Value of chain–length exponent b[12]					
	Range A: i=6–10		Range B: i=15–30		Range C: i=50–100	
MA	0.41	(±0.12)	1.14–1.15	(±0.08)	0.35–0.36	(±0.05)
EA	0.50–0.56	(±0.08)	1.12–1.14	(±0.05)	0.35–0.37	(±0.06)
BA	0.80–0.85	(±0.09)	1.14–1.18	(±0.06)	0.17–0.19	(±0.07)

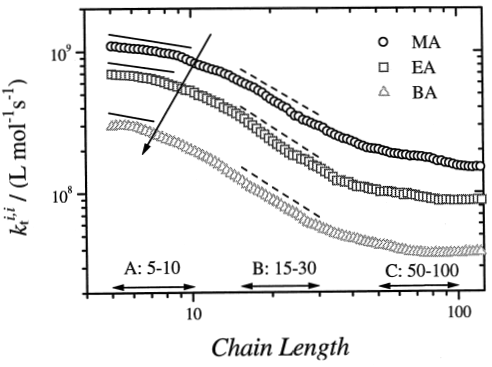

Figure 2. Termination rate coefficient vs. chain-length for three acrylates (methyl, ethyl and butyl acrylate) on a double logarithmic scale (25°C).

3) $\overline{k_t^m}$ *(a) and* $\overline{k_t^*}$ *(b) methods*

Methods 3a and 3b were applied to a number of systems, in particular styrene (St) in bulk[22,23] (25-70°C), shown in Figure 3, methyl methacrylate (MMA) in bulk[24,25] (25-70°C), styrene in various solvents[26] (toluene, ethyl acetate, cyclohexane and bis(3,5,5-trimethylhexyl-)phthalate). The results are always presented in a form analogous to Eqs.(17a) and (17b)

$$\overline{k_t^*} = A^{(*)} \cdot (\nu')^{-b} \tag{17c}$$

$$\overline{k_t^m} = A^{(m)} \cdot (\nu')^{-b} \tag{17d}$$

They can be summarized as follows (Table 2): In bulk a moderate chain-length dependence is observed at low temperatures (25°C) for St as well as MMA ($b \approx 0.18$). With increasing temperature, parameter b decreases significantly for St as well as for MMA finishing at $b \approx 0.10$ at 70°C. In an 1:1 mixture of St with good solvents (toluene, ethyl acetate, 25°C) the exponent is somewhat larger than in bulk polymerization, it is, however, definitely smaller in the bad solvents cyclohexane and bis(3,5,5-trimethylhexyl-) phthalate where it is in the range of about 0.10–0.13. In most cases the

agreement between the two methods satisfactory although – as predicted by theory – $\overline{k_t^m}$ is always a little smaller than $\overline{k_t^*}$, the $\overline{k_t^*}$ data moreover being less sensitive toward unfavorable factors such as chain transfer etc.

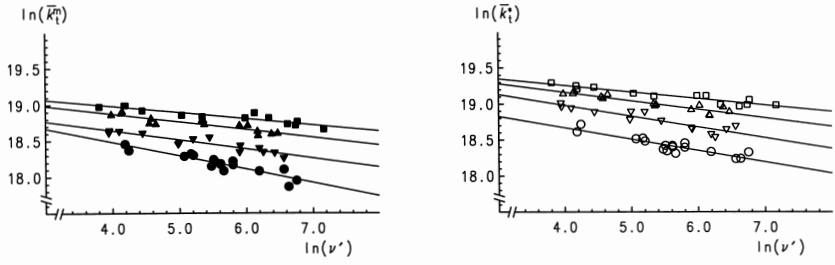

Figure 3. Double logarithmic plots of $\overline{k_t^m}$ and $\overline{k_t^*}$ vs. ν' at 25°C (●, ○), 40°C (▼, ▽), 55°C (▲, △) and 70°C (■, □) for bulk polymerization of styrene.[23]

Neither method 3a nor method 3b gives any indication of a dramatic change of b for small chain-lengths as reported with SP-PLP-MWD. It should be borne in mind, however, that the lowest ν' values (average lengths of terminating radicals) are not below 100 so that there can be no real chance of detecting such a feature.

It should be noted that the two methods are not necessarily restricted to pseudostationary polymerization (although it is advisable to use pseudostationary techniques because k_p data originating from these methods are needed anyway for the calculation of k_t) but might be easily adapted for stationary polymerization, too.[25] In this case $\overline{k_t^m}$ is evaluated according to Eq.(13) as before (but now from rate and $\overline{P_w}$ data obtained in

Table 2: Compilation of the results obtained by means of the different methods (A and b being the parameters contained in Eqs.(17c) and (17d))[22,24,26]

monomer-solvent (1:1) 25°C	$\overline{k_t^m}$		$\overline{k_t^*}$		LF-PLP
	b	$\frac{A^{(m)}}{10^8 \cdot \mathrm{L \cdot mol^{-1} \cdot s^{-1}}}$	b	$\frac{A^{(*)}}{10^8 \cdot \mathrm{L \cdot mol^{-1} \cdot s^{-1}}}$	b
St–none (bulk)	0.19	2.25	0.16	2.43	0.20 – 0.24
St–ethyl acetate	0.29	4.67	0.27	6.42	0.28 – 0.32
St–toluene	0.25	3.28	0.22	4.43	0.23 – 0.26
St–cyclohexane	0.10	2.09	0.10	3.52	0.08 – 0.12
St–bis(3.5.5–trime-thylhexyl–)phthalate	0.14	1.23	0.12	1.17	____
MMA–none (bulk)	0.17	1.10	0.16	1.33	0.17 – 0.21

stationary experiments) while Eq.(15) is replaced by the familiar equation

$$\overline{k_t^*} = \frac{k_p^2}{\overline{P_n} v_p}[M]^2 \frac{2}{1+\delta} \qquad (22)$$

In fact, this procedure based on *stationary* experiments was adapted to the study of the copolymerization system MMA-St at 25°C where – much to our surprise – the methods 3a and 3b in their usual pseudostationary form did not work satisfactorily. b parameters are sensibly independent of composition here but come out somewhat smaller for the pure monomers than with the other methods ($0.09 \le b \le 0.14$) which might be caused by the different type of CLD of the growing chains. $\overline{k_t}$ exhibits a maximum at intermediate compositions of the monomer feed. Because b does not show much variation with composition this maximum must be attributed to the experimental pre-exponential factor $A^{(*)}$ or $A^{(m)}$, respectively.

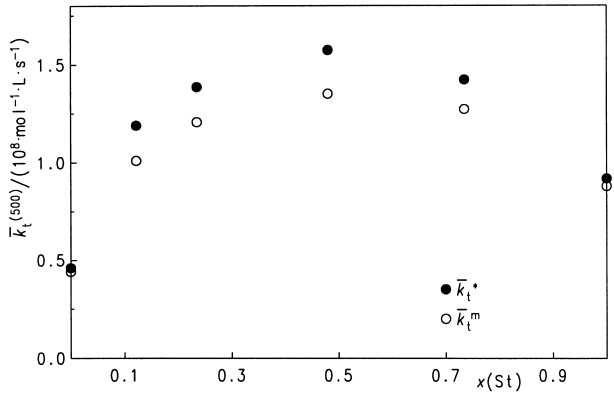

Figure 4. $\overline{k_t^m}$ and $\overline{k_t^*}$ determined for the stationary copolymerization of styrene (St) with methyl methacrylate (MMA) at 25°C.[25] The data refer to $\overline{P_n}$ = 500.

4) *LF-PLP*

This method[21] was applied to the same systems than the former ones, to some extent in order to check some of the more surprising results obtained.[22,24,26] Taken in all the b parameters obtained by methods 3a and 3b were fairly well reproduced (see also Table 2). Because the fit procedure is a rather sensitive one it takes a good part of the CLD from small chain-lengths upwards to obtain fairly constant parameters. Once the parameters are stable (i.e. they do not change on further extension of the range of the CLD to be fitted) the less interesting stable parameters a and c may be taken to try for a refined

fit for b either range by range (Figure 5, left part) or in a cumulative manner as before (Figure 5, right part). In either case[21] there are indications that b is sensibly higher for short chain-lengths starting with 0.75 for i = 100 (with huge error bars, however).

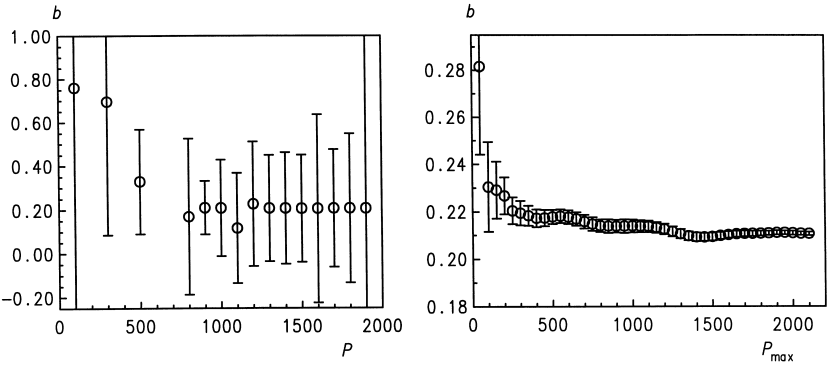

Figure 5. Parameter b determined from the CLD of polyMMA prepared by LF-PLP at 25°C.[21] Left diagram: range wise fit for $P \pm 100$. Right diagram: refined cumulative fit.

Discussion

It is difficult to compare the results obtained by SP-PLP-MWD to those originating from $\overline{k_t^m}$ and $\overline{k_t^*}$ methods or LF-PLP because they refer to different monomers as well as to different ranges of chain-lengths. The only common feature is that there is a moderate chain-length dependence for longer chains. In agreement with the data presented above such a moderate dependence has been found by Buback et al.[14] in the context of their analysis of TR-SP-PLP traces obtained by photolysis of a sensitizer yielding two radicals of widely different reactivity (2,2-dimethoxy-2-phenylacetophenone), i.e. 0.15 for St and 0.32 for MA. Before any attempt is made to discuss the overall chain-length dependences a short glance at the chain-length dependences of the individual steps involved in termination might be useful (Table 3).

According to this list the only exponent which comes close to those resulting from the last two methods (3 and 4) – to some extent also to one of the long chain values reported by de Kock (BA)[12] – is that caused by the "shielding effect" (entropic factor) which was established by simulations[29] for good and bad solvents (e.g. cyclohexane for polystyrene at 25°C) as well as by theoretical considerations, first for activation controlled reactions between chain ends[27] but later on shown to be valid also for reactions between end groups of high reactivity (radicals).[28] This agreement provides a

strong argument for the importance of this shielding effect in reactions between two coiled radicals. Changes in thermodynamic conditions might also be the reason for the decrease of parameter b observed with increasing temperature in bulk polymerization of St[23] and MMA.[25] It cannot be overlooked, however, that this shielding effect applies to radicals only which can be considered as coiled chains, a state which is reached after quite a number of propagation steps only. Accordingly, because the prefactors $A^{(*)}$ or $A^{(m)}$ in Eqs.(17c) and (17d) are the result of an extrapolation of the behavior of radical *chains* to unity degree of polymerization, they are not necessarily comparable with real $k_t^{1,1}$ values but rather represent the rate constant describing the termination between the hypothetical radicals of unity chain-length having all the properties of a (coiled) chain, however. From this point of view, therefore, at least two regimes of chain-length dependence have to be expected: a first one for small chain-lengths which is essentially controlled by translatorial diffusion ($0.5 \leq b \leq 0.6$) followed by another one dominated by the coiled-chain properties of the "grown-up" radicals. Although b obtained from SP-PLP-MWD at least approaches the conditions of a moderate chain-length dependence (but still being markedly in excess of 0.17) it is difficult at present – if not impossible at all – to give any reasonable explanation of these intermediate extremely high b parameters.

One point should be still added when discussing these results: Independently *which* of the methods introduced is applied all of them rely on a chain-length *independence* of k_p. This, however, has been put seriously to test quite recently: for a series of polymerization systems involving St and MMA as monomers it was found that k_p

Table 3: Chain-length dependence of the various steps involved in the termination process characterized by an exponent b in the power law $A \cdot i^{-b}$

Step	rate	athermal solvent	θ–solvent
Translatorial approach (center of mass diffusion)	?	0.6	0.5
Coil penetration (cooperative segment diffusion)	?	?	?
End-segment diffusion	?	0	0
Entropic factor (describing the shielding[29] of the chain-end by the rest of the chain)	—	0.17	0.05
Rotatory diffusion of terminal segments	fast	0	0
Chemical reaction	fast	0	0

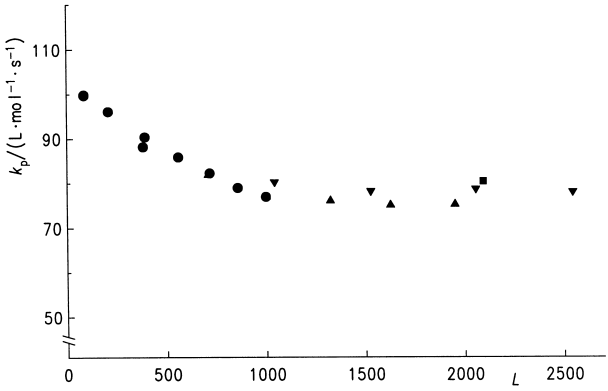

Figure 6. Experimental k_p data vs. chain-length for styrene polymerization in bulk at 25°C derived from first (●), second (▲), third (▼) and fourth (■) points of inflection.[30]

decreases markedly with chain-length[30] (see e.g. Figure 6). The quantitative consequences that this observation has for the evaluation of k_t cannot be estimated in full at present. Therefore only a preliminary assessment should be given for $\overline{k_t^m}$ and $\overline{k_t^*}$: For a wide range of chain-lengths k_p can be expressed by a power law

$$k_p^i = k_p^1 \cdot i^{-\beta} \tag{23}$$

where β is about 0.08. Using this dependence simulations of PLP were carried out with b=0.16 and b=0.24 as input values, respectively. The value of the b parameter returned from these simulations showed only a small deviation from the input values for the $\overline{k_t^*}$ method ($b = 0.15$ and $b = 0.23$, respectively) while this deviation was considerably larger for the $\overline{k_t^m}$ method ($b = 0.12$ and $b = 0.19$)[31] where the latter data might still improve if the range of chain-lengths examined is extended toward longer chains (Eq.(13) is strictly valid in the long-chain limit only). In view of these results the damage done to the methods of k_t evaluation by a nonlinear relationship between time and chain-length, which a non-constant k_p calls for, appears to be limited. Hopefully, the same result will be obtained for the SP-PLP-MWD and the LF-PLP method.

We are deeply indebted to Dr. John B. L. de Kock for the permission of using two figures from his thesis. Furthermore, we like to express our gratitude to him for critically proof-reading our description of the methods applied by him.
Support of this work by the Austrian Science Fund (Project #13114) and the Max-Buchner-Forschungsstiftung (Project #1842) is gratefully acknowledged.

[1] O. F. Olaj, A. Kornherr, G. Zifferer, *Macromol. Theory Simul.* **2000**, *9*, 131.
[2] K. C. Berger, G. Meyerhoff in *Polymer Handbook*, 3rd edition, J. Brandrup and E.H. Immergut, Eds., J.Wiley&Sons., New York **1989**, p.II/67ff.
[3] M. Kamachi, B. Yamada in *Polymer Handbook*, 4th edition, J. Brandrup, E.H. Immergut and A. Grulke, Eds., J. Wiley&Sons., New York **1999**, p.II/77ff.
[4] O. F. Olaj, I. Bitai, F. Hinkelmann, *Makromol. Chem.* **1987**, *188*, 1689.
[5] O. F. Olaj, I. Bitai, *Angew. Makromol. Chem.* **1987**, *155*, 177.
[6] M. Buback, L. H. Garcia-Rubio, R. G. Gilbert, D. H. Napper, J. Guillot, A. E. Hamielec, D. Hill, K. F. O'Driscoll, O. F. Olaj, J. Shen, D. Solomon, G. Moad, M. Stickler, M. Tirrell, M. A. Winnik, *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 293.
[7] M. Buback, R. G. Gilbert, G. T. Russell, D. J. T. Hill, G. Moad, K. F. O'Driscoll, J. Shen, M. A. Winnik, *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 851.
[8] M. Buback, R. G. Gilbert, R. A. Hutchinson, B. Klumperman, F.-D. Kuchta, B. G. Manders, K. F. O'Driscoll, G. T. Russell, J. Schweer, *Macromol. Chem. Phys.* **1995,** *196*, 3267.
[9] S. Beuermann, M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer, A. M. van Herk, *Macromol. Chem. Phys.* **1997**, *198*, 1545.
[10] M. Buback, H. Hippler, J. Schweer, H.-P. Vögele, *Makromol. Chem., Rapid Commun.* **1986**, *7*, 261.
[11] M. Buback, B. Huckestein, U. Leinhos, *Makromol. Chem., Rapid Commun.* **1987**, *8*, 473.
[12] J. B. L. de Kock, *Proefschrift*, Technische Universiteit Eindhoven, **1999**.
[13] J. B. L. de Kock, B. Klumperman, A. M. van Herk, A. L. German, *Macromolecules* **1997,** *30*, 6743.
[14] M. Buback, M. Busch, Ch. Kowollik, *Macromol. Theory Simul.* **2000**, *9*, 442.
[15] R. A. Lyons, J. Hutovic, M. C. Piton, D. I. Christie, P. A. Clay, B. G. Manders, S. H. Kable, R. G. Gilbert, *Macromolecules* **1966**, *29*, 1918.
[16] O. F. Olaj, G. Zifferer, *Eur. Polym. J.* **1989,** *25*, 961.
[17] O. F. Olaj, A. Kornherr, G. Zifferer, *Macromol. Chem. Phys., Rapid Commun.* **1997,** *18*, 997.
[18] O. F. Olaj, I. Bitai, G. Gleixner, *Makromol. Chem.* **1985,** *186*, 2569.
[19] O. F. Olaj, A. Kornherr, G. Zifferer, *Macromol. Chem. Phys., Rapid Commun.* **1998,** *19*, 89.
[20] O. F. Olaj, A. Kornherr, G. Zifferer, *Macromol. Theory Simul.* **1998**, 7, 501.
[21] O. F. Olaj, P. Vana, A. Kornherr, G. Zifferer, *Macromol. Chem. Phys,*. **1999**, *200*, 2031.
[22] O. F. Olaj, P. Vana, *Macromol. Rapid Commun.* **1998,** *19*, 433.
[23] O. F. Olaj, P. Vana, *J. Polymer Sci. Part A, Polymer Chemistry Ed.* **2000**, *38*, 697.
[24] O. F. Olaj, P. Vana, *Macromol. Rapid Commun.* **1998,** *19*, 533.
[25] O. F. Olaj, P. Vana, M. Zoder, to be published
[26] O. F. Olaj, P. Vana, M. Zoder, *Macromolecules* **2001**, *34*, 441.
[27] A. R. Khokhlov, *Makromol. Chem., Rapid Commun.* **1981**, *2*, 633.
[28] B. Friedman, B. O'Shaughnessy, *Macromolecules* **1993,** *26*, 5726.
[29] O. F. Olaj, G. Zifferer, *Makromol. Chem.* **1988,** *189*, 1097.
[30] O. F. Olaj, P. Vana, M. Zoder, A. Kornherr, G. Zifferer, *Macromol. Rapid Commun.* **2000**, *21*, 913.
[31] O. F. Olaj, A. Kornherr, G. Zifferer, *Macromol. Theory Simul.* **2001**, *10*, 881.