Is the rate constant of chain propagation \( k_p \) in radical polymerization really chain-length independent?

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**Introduction**

During the last few years, we have established three methods of estimating the chain-length dependence of the rate coefficient of bimolecular chain termination in radical polymerization \( k_t \).\(^{1-3} \) Two of them are based on equations referring to pulsed-laser polymerization (PLP), originally derived for chain-length independent termination, which now are used to define an average \( k_t \) to be assigned to the mean chain-length of the growing radicals at the moment of their termination. The first one, leading to an average \( k_m \), is the equation for the second moment of the chain-length distribution (CLD) – expressed by the product of rate of polymerization \( v_p \) and the weight-average degree of polymerization \( P_w \) – which was proved to be independent of initiation conditions\(^{4} \) (stationary or pseudostationary)

\[
P_w \cdot v_p = \frac{k_p^2}{k_t} [M]^2 (3 - \delta)
\]

with \([M]\) being the monomer concentration, \( k_p \) the rate constant of chain propagation, and the quantity \( \delta \) representing the contribution of disproportionation to overall termination.

The second one – defining an average \( k_1 \) – is the equation giving the rate of polymerization \( v_p \) in an experiment initiated by periodic laser pulses\(^{5} \)

\[
v_p = \frac{1}{t_0} \frac{k_p [M]}{k_t} \ln \left\{ 1 + \frac{\rho k_t t_0}{2} \left[ 1 + \left( 1 + \frac{4}{\rho k_t t_0} \right)^{1/2} \right] \right\}
\]

with \( \rho \) being the concentration of radicals produced in each pulse and \( t_0 \) the time elapsing between two pulses.

In principle, all the relevant quantities necessary for calculating \( k_m \) or \( k_1 \) – if not given by the experiment itself like \( t_0 \) – can be derived from the GPC-analysis of the polymer sample. Before all, this refers to the rate constant of chain propagation \( k_p \) which is necessary to isolate \( k_t \) in Eq. (1) and (2). Because the evaluation of \( k_1 \) as a function of chain-length necessitates quite a number of individual experiments for each system investigated and \( k_p \) can be evaluated from every individual experiment according to

\[
k_p = \frac{L_n^{(n)}}{n \cdot [M] \cdot t_0}
\]

where \( L_n^{(n)} \) is taken as the position of the \( n \)th point of inflection in the CLD.\(^{6,7} \) A lot of \( k_p \) data was accumulated automatically for each system. It is this method of determining

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**Communication:** A careful investigation of the \( k_p \) data obtained from pulsed-laser polymerization at different pulse separations \( t_0 \) in a lot of systems has revealed that \( k_p \) exhibits a slight but significant decrease when \( t_0 \) is increased, corresponding to an about 20% decrease of \( k_p \) extending over several hundreds in degree of polymerization. Transformation of this integral effect to individual chain-lengths reduces this range, of course, but still shows more than one hundred propagation steps to be concerned. This is interpreted in terms of a decrease of the monomer concentration at the site of propagation caused by the segments already added to the growing chain.
Experimental part

Materials

Styrene and MMA were purified by distillation under an atmosphere of nitrogen under reduced pressure and over an inhibitor remover (Aldrich, tert-butylcatechol-remover for styrene, hydroquinone remover for MMA). The photoinitiator benzoin, applied in concentrations between 0.2 and 1.5 $\times$ 10$^{-3}$ mol/L (slightly depending on the system) was recrystallized twice from ethanol. Tetrahydrofuran (THF) for GPC measurements was refluxed over potassium, distilled, and stabilized with 2,6-di-tert-butyl-p-cresol. Solvents (reagent grade) were distilled under nitrogen before being admixed to the purified monomers.

Polymerizations

The preparation of the samples was the same as described previously.$^{[1,2]}$

Analysis

Directly after laser irradiation (Nd:YAG Quanta Ray GCR-130-20 operated at 355 nm), the sample was mixed with a small amount of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) to prevent further polymerization, the monomer was evaporated, and the polymer diluted with THF to a concentration of $\approx$ 3 mg/mL. Then a GPC analysis was performed to obtain accurate molecular weight distributions.

The recording, transformation, and evaluation of the data was performed with the aid of a data manager (Viscotek DM 400) and the TriSEC® GPC software (version 3.0), conventional GPC module and data acquisition module, V2.70 (Viscotek). In order to calculate an accurate molecular weight distribution, polystyrene and poly(MMA) standards of low polydispersity were used. The evaluation of the calibration function of the GPC system and the computation of the CLD was accomplished by means of the TriSEC® GPC software.

For the estimation of the points of inflection, the GPC distribution was further subjected to the S.C.A.D.A. software (STV Computer Aided Data Acquisition, version 5.99, © J. Theiner). The GPC distribution was converted into a chain length distribution, thus transforming the x-axis into an axis linear in the degree of polymerization. The CLD was then differentiated by using a Savitzky-Golay algorithm$^{[23]}$ (with 11 supporting points). The maxima of the first derivative yield the appropriate chain length $L_0^p$ corresponding to the $n^0$ inflection point of the CLD and according to Eq. (3) also the $k_p$ value.

Curve fitting procedures

All the necessary multi-parameter nonlinear regressions were carried out with Prism 3.00, by GraphPad® Software.

Results and discussion

In order to give an impression of the shape of the GPC-traces, the mass and the number distribution of PLP-prepared polymers, a characteristic example (styrene in bulk) is given in Fig. 1 a–c. This should further demonstrate the experimental result that the second points of inflection – regardless which type of distribution is used for the evaluation of the points of inflection – are located at less than double the chain-lengths found for the first points of inflection invariably leading to a smaller $k_p$, according to Eq. (3) than it was obtained from the first points of inflection.

In Fig. 2a–e the results obtained for the systems

a) methyl methacrylate in bulk
b) styrene in bulk
c) styrene (1:1) in toluene
d) styrene (1:1) in cyclohexane
e) styrene (1:1) in ethyl acetate

are shown.

Invariably over all systems, a decrease of $k_p$ values with increasing $L_0$ is observed which amounts to about 20%. In the systems (a) and (b) where a particularly wide range of $L_0$ values was accessible, a slight tendency of a re-increase of $k_p$ at high $L_0$ can be noticed. As these data at high $L_0$ values are mostly derived from third and forth order points of inflection, the precision of which admittedly is somewhat inferior, we decided to omit these data from further discussion. As a consequence, we believe
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The main behavior to consist in a decrease of $k_p$, leveling off at higher $L_0$, thus finally attaining a constant value which is about 30–40% below the $k_p$ which would follow from an extrapolation to zero $L_0$. An indication of this  

Fig. 1. Pulsed laser polymerization of styrene in bulk at 25°C, $t_0 = 0.5$ s, monomer concentration 8.65 mol/L, sensitizer benzoin ($5 \times 10^{-3}$ mol/L), laser energy 40 mJ/pulse. Propagation constant $k_p$ ($k_p/L \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) from the positions of the first points of inflection: of GPC-trace (a) $L_0 = 354 \Rightarrow k_p = 81.9$; of mass distribution (b) $L_0 = 346 \Rightarrow k_p = 80.0$, of number distribution (c) $L_0 = 336 \Rightarrow k_p = 77.7$; from the positions of the second points of inflection: 2$L_0 = 659 \Rightarrow k_p = 76.2$ (a) 2$L_0 = 642 \Rightarrow k_p = 74.2$ (b) 2$L_0 = 639 \Rightarrow k_p = 73.9$ (c), respectively  

Fig. 2. Experimental $k_p$ data vs chain length for (a) methyl methacrylate in bulk, (b) styrene in bulk, (c) styrene (1:1) in toluene, (d) styrene (1:1) in cyclohexane and (e) styrene (1:1) in ethyl acetate derived from the first (○), second (△), third (▽) and fourth (■) point of inflection. For the evaluation of the corresponding integral function of $k_p$ (solid line) by curve fitting (Eq. (6b)), only $k_p$ data drawn from the first and second point of inflection were used. The extracted parameters of these fits were used to calculate the differential function of $k_p$ according to Eq. (6a), dashed line, the parameters being given in Tab. 1
behavior can be already derived from the data compiled in the benchmark paper referring to styrene,[9] looking at the data for 25 °C, those obtained for (the rather small) \( t_0 = 0.1 \text{ s} \), which correspond to a small \( L_0 \); accordingly, are markedly in excess over those which have been collected over a broad range of \( t_0 \) values \((0.2 \text{ s} \leq t_0 \leq 8 \text{ s})\). Analogous observations can be made for other temperatures, too. Thus the data obtained for 39.5 °C and \( t_0 = 0.1 – 0.2 \text{ s} \) equal those for 45 °C \((0.1 \text{ s} \leq t_0 \leq 10 \text{ s})\) and the same refers to the data at 50 °C \((t_0 = 0.1)\) and 55 °C \((0.1 \text{ s} \leq t_0 \leq 10 \text{ s})\). The situation is quite the same with respect to the 25 °C \( k_p \) data for the polymerization of methyl methacrylate.[9]

It cannot be completely excluded that the results are an artifact produced by the GPC-analysis or its calibration. Facing the fact that two completely different polymer systems like polystyrene and poly(methyl methacrylate) are under estimate \( L \) would implies that the situation would be completely neutral toward a variation of \( S \) or \( t_0 \).sarnecki and schweer[24] – based on the papers, [26] is taken as a means of assessing the situation [27] (otherwise second and even third or fourth order points of inflection would not have been detectable) where all the disturbing influences leading to a falsification of \( L_0 \) (if derived from the points of inflection) are minimum over a broad range of parameters.[27]

Finally, the observed effect certainly has nothing to do with the interaction of the fluctuation of propagation with chain-length dependent termination which should be rather weak and, moreover, should point into the opposite direction.[28] As a consequence, all the available material, if relevant at all, would rather point into the opposite direction.

When analyzing the situation it has to be considered that the \( k_p \) data for a certain \( L_0 \) in strict sense constitute average \( k_p \) values, \( F_0(L_0) \), taken over a range of chain-lengths between zero and \( L_0 \). The real interest, however, should concentrate on the instantaneous \( k_p(L) \) characterizing the propagation behavior of a chain of length \( L \). Quite generally, an instantaneous function of chain-length \( f(L) \) and the integral (average) function \( F(L) \) are interrelated by

\[
f(L) = L \cdot F'(L) + F(L) \tag{4a}
\]

where \( F'(L) \) is the first derivative of \( F(L) \) with respect to \( L \) based on an integral function defined by

\[
F(L) = L^{-1} \cdot \int_{0}^{L} f(L) dL \tag{4b}
\]

In order to get a first impression of how the instantaneous \( f(L) \) could look like, the experimental \( F_0(L_0) \) data were fitted according to

\[
F(L) = f(0) - a \cdot L/(L + b) \tag{5}
\]

which results in

\[
f(L) = f(0) - a \cdot (2bL + L^2)/(b + L)^2 \tag{5a}
\]

with \( a \) and \( b \) being constants and \( f(0) \) corresponding to the (hypothetical) propagation constant of a radical of zero chain-length. The plot of such an integral function (according to Eq. (5)) together with the calculated instantaneous \( k_p \) (Eq. (5a)) is shown as an example for one of these systems (system b) in Fig. 3. Although there is no justification for this specific choice of \( F(L) \) and not withstanding the fact that the instantaneous \( k_p \), of course, falls off much more rapidly than the integral one it is fair to conclude that the decrease must extend over quite a broad range of chain-lengths, thus indicating that the effect

![Fig. 3. The integral function of \( k_p \) (solid line) derived from experimental data (same as in Fig. 2b) by curve fitting according to Eq. (5) and the resulting differential function of \( k_p \) (Eq. (5a), dashed line) vs chain length \( L \) for styrene in bulk. Symbols as in Fig. 2](image-url)
cannot be restricted to a few degrees of polymerization only.

Facing this result it is very difficult to find an explanation. Of course, there are some hints in literature that propagation constants \( k_p \) are much elevated compared to \( k_p \) of a true chain radical for the very first growth-steps\(^{[29]}\). Contrarily to these rather strong effects that are restricted to a very narrow range, no indication whatsoever can be found, however, providing an explanation for this moderate long-range variation of chain-radical reactivity in an activation-controlled process such as chain-propagation. Looking at Eq. (3), however, it becomes evident that the quantity determined by measuring \( L_0 \) is not \( k_p \) but the product \( k_p[M] \) with \( k_p \) calculated from this product by dividing by the (nominal) macroscopic monomer concentration. This means that the long-range variation observed does not necessarily have its roots in a variation of \( k_p \), but may be traced back to a variation of the local monomer concentration at the site of reaction, i.e. in the close vicinity of the radical chain-end. The only reasonable way to imagine such a variation is that the segments already incorporated into the growing chain (more precisely the “tailing” rest of the chain) progressively displace part of the monomer molecules surrounding the radical chain-end where the propagation is to take place, until a certain limiting status is reached. In this way, the monomer units already added to the growing chain may reduce the probability of chain propagation pretending a decrease of \( k_p \) with increasing chain-length. Ideas of that type have already been put forward for the copolymerization of macromonomers of the MMA type with MMA where a model based on the segment density in the vicinity of the radical chain-end of the resulting comb polymer was successfully applied to explain the reactivity differences observed.\(^{[30]}\)

In order to get an impression of the scope of such an effect we have simulated self-avoiding chains on various lattice types, tetrahedral, cubic, cubic face-centered etc. Starting with the chain at a given lattice site, the next segment added occupies one of the \( Q \) co-ordination sites. It depends on the lattice type how many further segments have to be added until a further co-ordination site of the chain-end might be occupied. A plot of the fraction of unoccupied co-ordination sites around the chain-end, normalized to \( Q – 1 \), vs a modified chain-length \( L’ = L – 2 \) is shown for the cubic face-centered lattice (\( Q = 12 \)) in Fig. 4 (this modification is necessary because in this lattice, the first occupation of a lattice site adjacent to the chain-end is possible only for \( L = 3 \)). It can be seen that it takes quite a number of segments (about 50) until the asymptotic value is reached within small enough limits. Considering that one segment in a lattice chain corresponds to segments in an “equivalent” chain comprising about 15 monomer units this would mean that in real systems, the effect would come to a standstill only after a chain-length of about 750 (in the differential curve) is reached. There is some disappointment concerning the extent of the effect, however. As the extrapolation in Fig. 5 shows it cannot be expected that the effect will exceed 10% even for the highest co-ordinated lattices imaginable. This is admittedly lower by a factor three (or so) compared to the experimental results shown in Fig. 2a–e. The translation of these figures from a lattice system into an off-lattice real system in any case has to be considered with a good deal of reservation; off-lattice simulations may well offer results that are much closer to the experimental figures.

It is reasonable to assume that the instantaneous \( k_p \) represents the simpler function than the integral one. It is the integral function, however, which is the only experimentally accessible one. For this reason, we have calcu-
lated the associated integral functions if the instantaneous \( k_p \) follows a course indicated by Eq. (5)

\[
f(L) = f(0) - A \cdot L/(L + B)
\]

(with \( f(\infty) = f(0) - A \)) and for the case that the instantaneous \( k_p \) decreases exponentially towards a limiting value for large chain-lengths

\[
f(L) = (f(0) - f(\infty)) \cdot \exp\{-k \cdot L\} + f(\infty)
\]

The corresponding equations for the integral \( F_p(L_0) \) to be fitted to the experimental data are calculated to be

\[
F(L) = f(0) - A + A \cdot B \cdot L^{-1} \cdot \ln\{(B + L)/B\}
\]

for the first case and

\[
F(L) = (k \cdot L)^{-1} \cdot (f(0) - f(\infty)) \cdot (1 - \exp\{-k \cdot L\}) + f(\infty)
\]

for the second. Again \( A, B, \) and \( f(0) \) (for Eq. (6b)) and \( k, f(0), \) and \( f(\infty) \) (for Eq. (7b)) are parameters to be evaluated from a curve-fitting procedure.

For the differential (simulation) data presented in Fig. 4, the integral data can be calculated, too, of course. Thus, these data may serve to decide which is the best way of approximating the differential (lattice) data by a rather simple function, e.g. Eq. (6a) or Eq. (7a), and afterwards to check how well the corresponding integral function, Eq. (6b) or Eq. (7b), can represent the integral data. The intention is to apply the more suitable one out of these two (integral) functions to the experimental \( k_p \) data with the aim of calculating the individual function from the parameters of the integral one. An answer to this question is given by Fig. 6a and 6b which clearly show that the model based on a “Langmuir-like” approach to an asymptotic value, Eq. (6a) is superior to the exponential approach substantiated by Eq. (7a), not only with respect to the representation of the “experimental” points by the fitted curve but also concerning the quality of the representation of the course of the integral data by the fit parameters. This is corroborated by the data compiled in Tab. 1. Presuming this model to apply also to the \( L_0 \) dependence of \( k_p \), Eq. (6b) has been used throughout to fit the (real) experimental results and to calculate the dependence of the individual \( k_p \) values on \( L \) according to Eq. (6a) using the parameters extracted from this fit. These are summarized in Tab. 2. It is this function which is drawn as a broken line in Fig. 2a–e while the full curve corresponds to a fit of the integral data according to Tab. 1. Regression-parameters of the curves shown in Fig. 6 (plot vs. \( L' \)) for the simulated data in a cubic face-centered lattice, the quality of the fit indicated by the correlation coefficient \( R^2 \)

<table>
<thead>
<tr>
<th></th>
<th>( f(0) )</th>
<th>( f(\infty) )</th>
<th>( A )</th>
<th>( B )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated from the (Langmuir-like) differential function Eq. (6a)</td>
<td>0.9999</td>
<td>0.9125</td>
<td>0.0874</td>
<td>1.6574</td>
<td>0.99995</td>
</tr>
<tr>
<td>Calculated from the corresponding integral function Eq. (6b)</td>
<td>1.0022</td>
<td>0.9126</td>
<td>0.0896</td>
<td>1.5807</td>
<td>0.99997</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( f(0) )</th>
<th>( f(\infty) )</th>
<th>( k )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated from the (exponential) differential function Eq. (7a)</td>
<td>0.9904</td>
<td>0.9158</td>
<td>0.2728</td>
<td>0.95471</td>
</tr>
<tr>
<td>Calculated from the corresponding integral function Eq. (7b)</td>
<td>0.9858</td>
<td>0.9169</td>
<td>0.2606</td>
<td>0.99207</td>
</tr>
</tbody>
</table>
Eq. (6b), of course. The physical significance of the fit parameters should not be overrated, however. This is so for various reasons, among them the experimental scatter of the underlying data and, before all, because there is no really cogent physical foundation for the type of fit used. The long-range character of the effect is clearly evident in any case (parameter $B$ gives the chain-length where the decrease is half the difference between $k_p$ extrapolated to zero chain-length and $k_p$ extrapolated to infinite chain-lengths). It is somewhat surprising to find that the effect is a little less far-reaching for MMA than for the styrene systems although the opposite would be expected because of the greater stiffness of the PMMA chain, for reasons we cannot find out at the moment. It should not be overlooked in this context, however, that it is this system which exhibits the worst agreement (smallest correlation coefficient) with the model represented by Eq. (6b).

### Conclusions

The main conclusion to be drawn from the results of this communication is that the clock set by the propagation steps in radical polymerization does not work fully linear in time. This has serious implications for the kinetics and the evaluation of kinetic constants because most of these methods rely on the constancy and chain-length independence of $k_p$ or relate the other quantities to $k_p$. This refers to the determination of chain-transfer constants which are given as the ratio of the rate constant of chain transfer over the rate constant of chain propagation and, before all, refers to all methods of determining the rate constant of bimolecular termination. Thus, in strict sense, at least to some extent, not only the $k_i$ data obtained by application of Eq. (1) or Eq. (2) have to be revisited because they use a constant $k_p$, but also the data on the exponent $b$ in the power law that relates $k_i$ to the chain-length of the terminating radicals which is obtained by our third method. Even the ingenious method to calculate $k_i$ and its chain-length dependence range-wise from the CLD which was recently designed by de Kock (claimed to be model-independent) and the equally ingenious way of obtaining $k_i$ data from time-resolved conversion-time curves developed by Buback et al. will face the same problems when degree-of-polymerization scales have to be transformed into time scales or vice versa. The incorporation of a chain-length dependent propagation constant into any kinetic scheme (irrespective whether for steady-state or for pseudostationary polymerization) is by no means trivial partly because the chain-length dependence – contrarily to what appears to be the case with the termination coefficient – probably does not follow a simple power law. Simulations of the type carried out with respect to event-weighted terminations, now applied to propagation, too, hopefully may prove to be helpful in this field.

If the reason for the observed effect really consisted in a progressive shielding of the active center by the tailing rest of the growing chain then it should not be restricted to radical polymerization but should play an (independently observable) role also in polymerizations following different mechanisms especially if the polymerizations are living ones. Also in this case, deviations from the proportionality between time and chain-length should occur. Taken in all, quite a number of chapters of polymerization kinetics would have to be rewritten in this case.

Acknowledgement: This study is part of a project (# 13114-CHE) supported by the Austrian Science Fund which is gratefully acknowledged.

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Tab. 2. Regression-parameters of the curves shown in Fig. 2, the quality of the fit indicated by the correlation coefficient $R^2$

<table>
<thead>
<tr>
<th>System</th>
<th>$f(0)$</th>
<th>$A$</th>
<th>$B$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Poly(methyl methacrylate)</td>
<td>406.6</td>
<td>169.0</td>
<td>135.4</td>
<td>0.783</td>
</tr>
<tr>
<td>(b) Polystyrene</td>
<td>107.0</td>
<td>47.4</td>
<td>256.3</td>
<td>0.976</td>
</tr>
<tr>
<td>(c) Polystyrene/toluene</td>
<td>99.4</td>
<td>64.3</td>
<td>711.6</td>
<td>0.943</td>
</tr>
<tr>
<td>(d) Polystyrene/cyclohexane</td>
<td>112.7</td>
<td>54.1</td>
<td>468.0</td>
<td>0.850</td>
</tr>
<tr>
<td>(e) Polystyrene/ethyl acetate</td>
<td>90.5</td>
<td>35.0</td>
<td>200.2</td>
<td>0.874</td>
</tr>
</tbody>
</table>

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