# Chain Length Dependence of Chain Propagation Revisited

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ABSTRACT: On the basis of recently developed numeric procedures, the results obtained for the propagation constants $k_p$ by means of the PLP−SEC method (pulsed laser polymerization followed by size exclusion chromatographical analysis of the chain length distribution) were subjected to a critical reevaluation and reanalysis particularly with respect to the chain length dependence of $k_p$. In this context the errors arising from a broadening caused by axial dispersion in the SEC were largely eliminated together with other uncertainties in assessing the characteristic chain length $L_0$ on which the evaluation of $k_p$ is based. The main result that refers to the bulk polymerization of methyl methacrylate and styrene in the temperature range 25−70 °C is that the previously found negative long-range chain length dependence of $k_p$ survived this procedure to an extent that widely exceeds the known variation of $k_p$ for extremely short chains and extends over a range of several hundreds of propagation steps.

## Introduction

The treatment of the kinetics of free radical polymerization by textbooks usually relies on the chain length independence of the rate constant of chain propagation $k_p$ for several good reasons. First, such an assumption greatly simplifies establishing the kinetic scheme, second the kinetic scheme developed in this way was quite well verified by the experimental results originating from steady-state polymerization, and third, for a very long time even the $k_p$ data obtained for itself did not exhibit any feasible indications of a chain length dependence exceeding the appreciable experimental error associated with its determination.[1] From the chemical point of view it would not be unreasonable if there were a dependence restricted to the (very) first propagation step(s), $k_p^{(n)}$, $n$ being 1, 2, 3, etc. Two cases are to be distinguished: $k_p^{(1)} < k_p^{(\infty)}$ would correspond to retardation because the slow transformation of small into long chain radicals would give increased room to termination reactions. The other case, $k_p^{(1)} > k_p^{(\infty)}$, appears to be less problematic because the above-mentioned transformation occurs more rapidly compared to a situation with chain length independent $k_p$, the only consequence being slightly prolonged chain lengths and somewhat enhanced rates of polymerization.[2] Actually, it is the latter case that corresponds to reality as has been impressively demonstrated by Gridnev and Ittel[3a] who among others[3b] found that $k_p^{(1)}$ might exceed $k_p^{(\infty)}$ by a factor of 10 or more. These observations, however, were definitely restricted to extremely short radicals. First indications of a *long range* chain length dependence of $k_p$ came up after the method of directly determining this quantity[4] had promoted into a IUPAC-recommended procedure.[5] In this method, later on named PLP−SEC (pulsed laser polymerization followed by an evaluation of the chain length distribution by size exclusion chromatography), a photopolymerizable system is subjected to periodic laser pulse initiation and $k_p$ is determined from a characteristic chain length $L_0$ (or one of its “multiples” $L_0^{(n)}$, $n \geq 2$) to be extracted from the (rather complicated) chain length distribution (CLD) of the resulting polymer that in the simplest cases is given by the equation derived by Aleksandrov et al. either in its original[6] or in its revised form.[7] $L_0$ *and* $L_0^{(n)}$, respectively, are related with $k_p$ by

$$k_p = L_0/([\mathrm{M}]t_0) \tag{1}$$

$$k_p = L_0^{(n)}/(n[\mathrm{M}]t_0) \tag{1a}$$

where [M] is the monomer concentration and $t_0$ is the length of one period (reciprocal laser frequency). Unfortunately, because of the genuine Poissonian broadening to which individual degrees of polymerization $l$

$$l = k_p[\mathrm{M}]t \tag{2}$$

corresponding to a lifetime $t$ are subjected, $L_0$ does not appear in the CLD as a discontinuity (reflecting the instantaneous increase of termination probability due to the radicals newly produced in every incoming laser pulse). Actually, the discontinuity is transformed into a (usually) steep ascent followed by a maximum forming a so-called “extra peak”.[4] For the majority of experimental conditions the position of the point of inflection $l_{\mathrm{LPI}}$ on the low molecular side of the peak in the vicinity of $L_0$ proved to be the best substitute for $L_0$[4,8] although the position of the maximum $l_{\mathrm{MAX}}$ is occasionally favored[9] which, however, is justified for high concentrations of primary radicals $\rho$ formed by each laser pulse only.[8] A description of the overall situation together with sketches of the CLD can be found in previous publications.[4,9]

On the basis of taking $l_{\mathrm{LPI}}$ as a substitute for $L_0$ a careful analysis of data revealed the existence of a distinct *long range* chain length dependence of $k_p$ extending over hundreds of degrees of polymerization[10,11] in the polymerization of styrene (in bulk and in solution) as well as in the polymerization of methyl methacrylate (in bulk) that was explained by a progressive decrease of local monomer concentration at the site

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of propagation (actually, it is the product $k_p[\mathrm{M}]$ which is determined via eq 1 from which $k_p$ may be derived by dividing this product by the nominal overall monomer concentration). Admittedly, there is a further problem in the evaluation of $L_0$ or $L_0^{(n)}$, respectively. This is inherent in the SEC technique used in the analysis of the CLD and consists of the Gaussian broadening caused by the axial dispersion that similar to the genuine Poisson broadening affects the positions of $l_{\mathrm{LPI}}$ and $l_{\mathrm{MAX}}$ (relative to $L_0$) which might lead to falsifications in $k_p$ if these are uncritically taken as substitutes for $L_0$. For these reasons, we developed correction functions for the experimentally determined $l_{\mathrm{LPI}}$ and $l_{\mathrm{MAX}}$, based on simulated CLDs subjected to Poissonian and various degrees of Gaussian broadening, to obtain $L_0$ and as a consequence $k_p$ data that are essentially free of the errors introduced by the various broadening effects. These corrections were primarily applied to the first extra peak,[12,13] but finally extended also to higher order points of inflection and higher order maxima[14] ($n \geq 2$). Thus, a powerful tool for a reinvestigation of our older data on the chain length dependence of $k_p$ is at disposition. This reanalysis is the first attempt to eliminate *all* the shortcomings connected with the analysis of PLP samples by SEC and therefore should answer the question whether our previous observations concerning this subject are indeed real or are due to artifacts produced by Poissonian and especially Gaussian broadening on the CLDs of PLP-produced polymers as was recently put forward.[15,16] To demonstrate the most essential points only, we will confine ourselves to data of polymerization of styrene (St) and methyl methacrylate (MMA) at various temperatures.[10,11]

## Procedure

Subjects of the reanalysis were the hyper mass distributions $w^{\mathrm{SEC}}$ obtained by SEC as a function of chain length $l$ assessing the position of the maximum $l^{(n)}_{\mathrm{MAX}}$ as well as the positions of the points of inflection on the low molecular ($l^{(n)}_{\mathrm{LPI}}$) and the high molecular weight ($l^{(n)}_{\mathrm{HPI}}$) side of the maximum. $l^{(n)}_{\mathrm{LPI}}$ and $l^{(n)}_{\mathrm{HPI}}$ define the (experimental) width of the peak $\delta_{\mathrm{E}}$[17]

$$\delta_{\mathrm{E}} = \frac{l_{\mathrm{HPI}}}{l_{\mathrm{LPI}}} \tag{3}$$

This quantity is to be compared to a (theoretical) width $\delta_{\mathrm{T}}$ composed of the width of a Poissonian peak at $l^{(n)}_{\mathrm{MAX}}$, $\delta_{\mathrm{P}}$

$$\delta_{\mathrm{P}} = \frac{l_{\mathrm{MAX}} + \sqrt{l_{\mathrm{MAX}}}}{l_{\mathrm{MAX}} - \sqrt{l_{\mathrm{MAX}}}} \tag{4}$$

subjected to a Gaussian broadening of intensity $\sigma_{\mathrm{ad},k}$[12-14,18,19]

$$\delta_{\mathrm{T}} = 10^{\sqrt{lg^2\delta_{\mathrm{P}} + 4\sigma_{\mathrm{ad},k}{}^2}} \tag{5}$$

where additivity of variances has been assumed. For a given $\sigma$ (the subscript being omitted now), which can be rather easily determined for each SEC device,[18,19] the correction factors $L_0/l_{\mathrm{LPI}}$ and $L_0/l_{\mathrm{MAX}}$ for first order points of inflection and first-order maxima as well as correction factors for higher order points of inflection $l^{(n)}_{\mathrm{LPI}}$ and higher order maxima $l^{(n)}_{\mathrm{MAX}}$ in general can be well represented by linear relationships[12-14]

$$f^{(n)}_{\Theta,\mathrm{LPI}} = L_0^{(n)}/l^{(n)}_{\mathrm{LPI}} = I - S\Theta \tag{6}$$

$$f^{(n)}_{,\Theta\mathrm{MAX}} = L_0^{(n)}/l^{(n)}_{\mathrm{MAX}} = I - S\Theta \tag{7}$$

with $\Theta$ being one of the two functions

$$X \equiv \lg^2\delta_{\mathrm{E}} - \lg^2\delta_{\mathrm{T}} \tag{8}$$

$$Y \equiv (\delta_{\mathrm{E}} - 1)/(\delta_{\mathrm{T}} - 1) - 1 \tag{9}$$

and $I$ and $S$ being intercepts and slopes in these relationships.[12-14] Thus, the general procedure of obtaining $k_p$ data widely free of falsifications caused by Gaussian (and also Poissonian) broadening is as follows:

(a) to analyze the experimentally obtained CLD for $l^{(n)}_{\mathrm{MAX}}$, $l^{(n)}_{\mathrm{LPI}}$, and $l^{(n)}_{\mathrm{HPI}}$,

(b) to calculate $\delta_{\mathrm{E}}$, $\delta_{\mathrm{P}}$, and (for a known or previously evaluated axial dispersion parameter $\sigma$) also $\delta_{\mathrm{T}}$,

(c) to establish the value of function $X$ or $Y$ from $\delta_{\mathrm{T}}$ and $\delta_{\mathrm{E}}$,

(d) to calculate the correction factors $f^{(n)}_{\Theta,\mathrm{LPI}}$ and $f^{(n)}_{\Theta,\mathrm{MAX}}$ ($n = 1,2...$; $\Theta = X, Y$), and finally

(e) to evaluate corrected values of $L_0$, $L_0^{(2)}$, $L_0^{(3)}$ etc. (multiplying $l^{(n)}_{\mathrm{LPI}}$ and $l^{(n)}_{\mathrm{MAX}}$ by the respective correction factor), to transform them into $k_p$ data and to associate them with the chain lengths to which they refer.

Of course, only those peaks can be treated for which *all* the three quantities enumerated in item a can be determined.

In particular, termination in methyl methacrylate was treated as being exclusively by disproportionation while combination was the mode of termination assumed for styrene. The correction function $X$ was used throughout taking $\sigma = 0.05$ (function $Y$ would yield similar results). This is a common figure for SEC-systems consisting of four 10 $\mu$m columns of 30 cm length ($10^3$, $10^4$, $10^5$, and $10^6$ Å, Polymer Standards Service). For convenience of the reader the parameters $I$ und $S$ actually used in the present communication for first[13] and second[14] order peaks are summarized in Table 1.

Sample preparation was already described in previous communications.[10,11] The algorithm used for carrying out the multiparameter fit procedures (nonlinear regressions) was the same as used previously[10,11] (Prism 3.00, by GraphPad Software).

## Results

At first, the basic effect produced by applying the corrections is demonstrated in Figure 1a for a selected example (methyl methacrylate in bulk, 25 °C). In a plot of $k_p$ vs $l$ data points originating from $l^{(n)}_{\mathrm{LPI}}$ are shifted upward (higher $k_p$) and slightly to the right (higher $L_0$) whereas the reverse is true for data derived from $l^{(n)}_{\mathrm{MAX}}$. The main point, however, is that, on the whole, all data now *coincide* independently from which source they were obtained. Of course, the new function (full line) that makes use of corrected $l^{(n)}_{\mathrm{LPI}}$ as well as of corrected $l^{(n)}_{\mathrm{MAX}}$ data is shifted upward compared to the older representation that had been exclusively based on (uncorrected) points of inflection[10] (dotted line). This implies that the $k_p$ data in our previous communications[10,11] have generally been too small. With respect to the overall picture, however, there is no substantial change which means that a substantial long-range chain length dependence of $k_p$ *persists* even *after* having corrected for the distortions caused by the chosen

**Table 1. Parameters $I$ and $S$ ($\sigma = 0.05$)**

| mode of termination | $n$ | $L_0^{(n)}/l^{(n)}_{\mathrm{LPI}} = I - SX$ | | $L_0^{(n)}/l^{(n)}_{\mathrm{MAX}} = I - SX$ | |
|---|---|---|---|---|---|
| | | $I$ | $S$ | $I$ | $S$ |
| disproportionation | 1[a] | 1.118 | 6.8 | 0.998 | 19.7 |
| | 2[b] | 1.074 | 3.7 | 0.924 | 16.5 |
| combination | 1[a] | 1.104 | 7.4 | 0.982 | 19.9 |
| | 2[b] | 1.090 | 11.8 | 1.002 | 41.9 |

[a] Taken from Table 1 of ref 13. [b] Calculated from master functions given in ref 14.

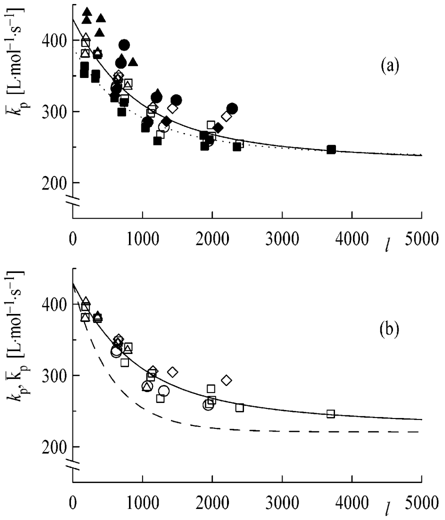

**Figure 1.** Polymerization of methyl methacrylate in bulk at 25 °C. (a) Filled symbols refer to uncorrected experimental data and open symbols to corrected ones: squares, first points of inflection; rhombi, second points of inflection; triangles, first maxima; circles, second maxima. Full curve: "integral" fit function according to eq 12 for corrected points. Dotted curve: "integral" fit function according to eq 12 for uncorrected $l_{\mathrm{LPI}}$ data. (b) Full curve: "integral" fit function for corrected points (as in Figure 1a). Dashed curve: "differential" function according to eq 12a reconstructed from the parameters found for the integral fit function.

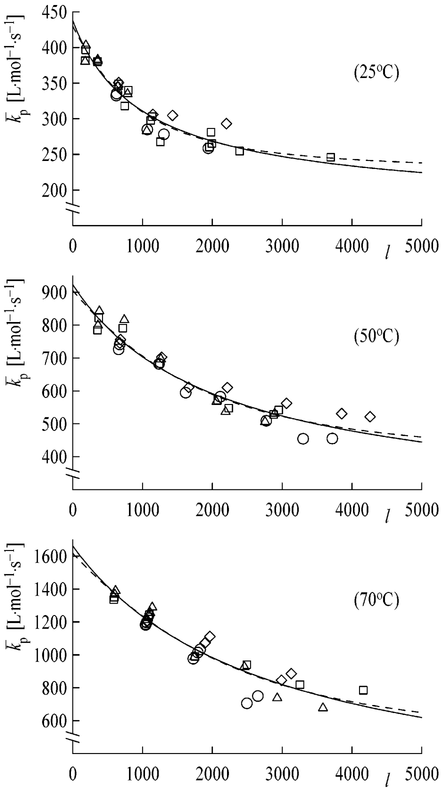

**Figure 2.** Temperature and chain length dependence of the propagation coefficient of methyl methacrylate based on corrected data. Symbols are as in Figure 1. Curves for integral fit functions: full line, "Langmuir", eq 11; dashed line, "exponential", eq 12.

method of instrumental analysis (SEC). Of course, there is noticeable scatter of the data left but it should be kept in mind that only the error due to the replacement of $L_0$ by $l_{\mathrm{LPI}}$ has largely been eliminated whereas all the other experimental and instrumental errors inherent in the determination of $l_{\mathrm{LPI}}$ and $l_{\mathrm{MAX}}$ are still operative.

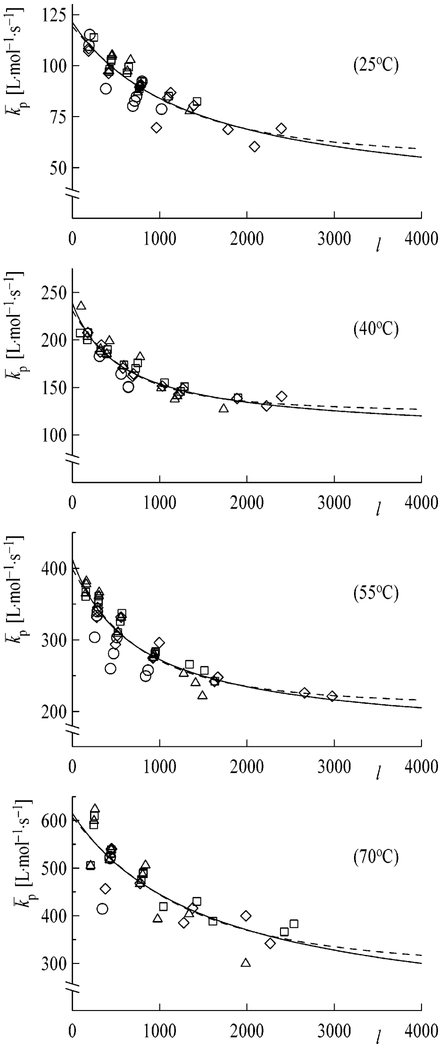

**Figure 3.** Temperature and chain length dependence of the propagation coefficient of styrene, corrected data. Symbols and curves are as in Figure 2.

Figures 2b,c and 3a–d, which refer to MMA (50, 70 °C) and St (25, 40, 55, 70 °C), respectively, essentially transmit the same impression that has been conveyed by the selected example discussed above, Figure 1a, for convenience repeated as Figure 2a in a different context.

## Discussion

The $k_p$ data shown in Figures 1–3, which were all calculated on the basis of eqs 1 and 1a, respectively, in essence represent $\overline{k}_p$ values averaged over the time that elapses between chain initiation and time $nt_0$ in which latter instant they have reached a chain length of $L_0^{(n)}$. More interesting than these averaged or integral data, however, are the *individual* or *differential* values of $k_p$ referring to *individual* degrees of polymerization. In principle, their determination could be accomplished by graphical or numerical differentiation of the function $\overline{k}_p$ versus $l$. Because of the experimental scatter, it is preferable to fit the integral data to a model function and to subsequently calculate the individual $k_p$ data from the parameters of that function. On the basis of rather simple differential functions (eqs 11a and 12a) the following integral functions were derived

$$\text{(a)}\quad \overline{k_p}(l) = (k_p(0) - A) \times \left[1 - \frac{AB}{(k_p(0) - A)l}\ln\left(\frac{(k_p(0) - A)l}{Bk_p(0)} + 1\right)\right]^{-1} \tag{11}$$

$$\text{(b)}\quad \overline{k_p}(l) = klk_p(\infty) \times \left[\ln\left(\frac{(k_p(0) - k_p(\infty))}{k_p(0)} + \frac{k_p(\infty)}{k_p(0)}e^{kl}\right)\right]^{-1} \tag{12}$$

For function a, this is an individual function mimicking the Langmuir adsorption isotherm, starting with $k_p(0)$ and tending toward a limiting value $k_p(\infty) = k_p(0) - A$, with the parameters $k_p(0)$, $A$, and $B$

$$k_p(l) = k_p(0) - \frac{A}{B + l}\, l \tag{11a}$$

Function b relies on a differential function that decays exponentially from $k_p(0)$ to $k_p(\infty)$ (parameters $k_p(0)$, $k_p(\infty)$, $k$)

$$k_p(l) = (k_p(0) - k_p(\infty))\exp\{-kl\} + k_p(\infty) \tag{12a}$$

Both functions a and b try to account for the displacement of monomer by polymer segments in the vicinity of the active site in the course of chain growth.

The parameters for all systems under investigation are compiled in Table 2 (a-lines), which additionally contains the parameters characterizing data based on uncorrected $l_{\mathrm{LPI}}^{(n)}$ values (b-lines) for comparison.[10,11] The difference between "integral" and "differential" function is demonstrated in Figure 1b using the exponential model, eqs 12 and 12a, again for the system MMA at 25 °C, the full curve fitted according to eq 12, the dotted curve representing eq 12a. Of course, the decay of the individual function is restricted to a much smaller range of chain lengths than for the integral functions but is still remarkable. The two extrapolated quantities $k_p(0)$ and $k_p(\infty)$ differ by a factor of almost 2 (the highest and the lowest experimentally found values still by a factor of 1.5, after all). Accordingly it takes about 500 propagation steps for $k_p(l)$ to drop from $k_p(0)$ to $k_{p,1/2} \equiv (k_p(0) + k_p(\infty))/2$ indicating the existence of a considerable long-range chain length dependence of $k_p$. It would be comparatively easy to separate this long-range chain length dependence of $k_p$ from the "short chain" anomaly[3] of $k_p$ because they occur in fully different chain length regimes and the short-range effects would result in a shift of a few units along the $l$ axis only.[2] However, the extrapolated $k_p(0)$ data obtained in this work by the multiparameter fit procedures will admittedly not be representative of the real propagation constant of those extremely short chains.

Figures 2 and 3 additionally show the fits that are obtained for the two models described above in their integral representation, eqs 11 and 12. From visual inspection as well as from the correlation coefficients $R^2$ (Table 2) it can be concluded that there are no great differences (at least in the accessible range of chain lengths) so that no marked preference for one of the models (a or b) can be expressed. It is common for both models, however, that, for all investigated systems, they still argue in favor of a marked wide range decay of $k_p$ that extends over hundreds of monomer units, even after transformation into the representation of individual (unaveraged) $k_p$ data—eqs 11a and 12a. Information on this behavior might be inferred from a quantity $L_{1/2}$ that is the chain length for which the decay of the individual $k_p$ with chain length is half complete within the frame of the model ($k_p(L_{1/2}) \equiv k_{p,1/2}$).

The influence that is exercised by applying the corrections can be additionally extracted from Table 2 by comparing the a-lines (corrected data) to the b-lines (uncorrected data). $k_p(0)$ is generally increased whereas $k_p(\infty)$ is rather decreased, thus extending the span between the two quantities.

In our former communication on this subject[11] the results were additionally analyzed according to a third model that was based on a power law dependence of $k_p$ on chain length introduced into this subject long ago[20]

$$k_p(l) = k_p(1)l^{-\alpha} \tag{13a}$$

Because of the rather unphysical nature of this model ($k_p(\infty)$ in this case may become zero for infinite chain lengths) and the lower correlation coefficients obtained in comparison to models a and b, its application is not further pursued in the present communication. With respect to the range of the chain length dependence of $k_p$ (expressed by the quantity $L_{1/2}$) the application of the corrections rather produced an increase, thus even emphasizing the long range character of the effect. It should be noted, however, that in the new fit procedure only those data were included for which the necessary conditions for carrying out the corrections were fulfilled;

**Table 2. Fit Parameters for the Investigated Systems ($k_p(0)$, $k_p(1)$, $k_p(\infty)$, $k_{p,1/2}$, and $A$ in [L mol$^{-1}$s$^{-1}$], Where All the Other Parameters Are Nondimensional)**

| system | | "Langmuir" eqs 11 and 11a | | | | | | "exponential" eqs 12 and 12a | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $k_p(0)$ | $k_p(\infty)$ | $A$ | $B = L_{1/2}$ | $k_{p,1/2}$ | $R^2$ | $k_p(0)$ | $k_p(\infty)$ | $k/10^{-3}$ | $L_{1/2}$ | $k_{p,1/2}$ | $R^2$ |
| MMA 25 °C | a | 438.2 | 165.7 | 272.5 | 517.4 | 350.7 | 0.9145 | 429.9 | 220.8 | 1.831 | 378.6 | 369.2 | 0.9220 |
| | b | 398.9 | 190.2 | 208.7 | 416.7 | 332.4 | 0.9214 | 390.2 | 226.9 | 2.066 | 335.5 | 343.1 | 0.9302 |
| MMA 50 °C | a | 923.7 | 208.0 | 715.7 | 1091.0 | 690.6 | 0.9272 | 905.8 | 375.9 | 0.951 | 728.8 | 750.6 | 0.9319 |
| | b | 819.6 | 316.7 | 502.9 | 746.5 | 658.2 | 0.9250 | 802.3 | 418.8 | 1.260 | 550.1 | 691.1 | 0.9341 |
| MMA 70 °C | a | 1662.8 | 112.3 | 1635.6 | 1402.4 | 1118.6 | 0.9015 | 1618.0 | 437.0 | 0.766 | 904.9 | 1266.9 | 0.9042 |
| | b | 1407.4 | 156.5 | 820.1 | 568.9 | 1144.8 | 0.9586 | 1321.5 | 683.6 | 0.113 | 612.3 | 1136.5 | 0.8357 |
| St 25 °C | a | 121.3 | 27.5 | 93.8 | 723.1 | 90.8 | 0.8037 | 119.2 | 50.8 | 1.495 | 463.6 | 99.2 | 0.8030 |
| | b | 124.6 | 67.5 | 57.1 | 134.9 | 106.5 | 0.8713 | 115.3 | 72.7 | 3.879 | 178.7 | 103.1 | 0.8939 |
| St 40 °C | a | 238.7 | 95.4 | 143.3 | 293.7 | 192.7 | 0.8930 | 230.9 | 119.5 | 2.792 | 248.3 | 198.6 | 0.8949 |
| | b | 213.3 | 113.4 | 99.9 | 224.9 | 181.6 | 0.9425 | 207.1 | 128.0 | 3.386 | 204.7 | 184.4 | 0.9550 |
| St 55 °C | a | 412.9 | 152.2 | 260.7 | 379.6 | 329.1 | 0.8451 | 399.2 | 199.1 | 2.238 | 309.7 | 341.1 | 0.8453 |
| | b | 385.8 | 192.8 | 193.0 | 253.8 | 324.4 | 0.9023 | 371.1 | 219.7 | 2.859 | 242.4 | 327.5 | 0.9138 |
| St 70 °C | a | 614.9 | 149.8 | 465.1 | 831.7 | 463.7 | 0.7329 | 606.9 | 269.6 | 1.352 | 512.7 | 508.4 | 0.7354 |
| | b | 614.1 | 343.0 | 271.1 | 194.6 | 528.3 | 0.7424 | 580.3 | 373.2 | 3.125 | 221.8 | 520.9 | 0.7535 |

[a] Fit parameters referring to corrected data (first and second LPIs as well as first and second MAX). [b] Fit parameters referring to uncorrected data (only first and second LPIs that satisfied the necessary preliminaries for correction).

thus, the b-lines do not exactly correspond to the previously published data.[10,11]

Quite recently, Willemse et al. performed studies on the same topic (chain length dependence of $k_p$ in styrene and methyl methacrylate bulk polymerization), investigating a similar temperature range in the case of styrene (20−60 °C) and concentrating on lower temperatures in the case of methyl methacrylate (−18 to +25 °C). They also employed the PLP technique for sample preparation, but analyzed the CLDs by MALDI−ToF−MS (matrix assisted laser desorption ionization−time-of-flight−mass spectrometry).[15] Relying on $l_{MAX}$ (referring to a number distribution in this case, of course) as a substitute for $L_0$ and using eq 1, they arrived at the conclusion that the variation of $k_p$ is restricted to the extreme oligomeric range ($l$ at most 5−10) and claimed the long-range variation of $k_p$ as being an artifact due to instrumental effects in SEC (column band broadening by axial dispersion). Without entering into a thorough discussion on the advantages and disadvantages of the two methods (MALDI−ToF−MS on the one side and SEC on the other) there is serious concern in the literature about MALDI being an appropriate tool for determining complete chain length distributions of polymers. It may suffer from “mass discrimination”, both with respect to desorption−ionization and with respect to detection,[21,22] even if an improved matrix material has been used. This mass discrimination might easily cause delicate falsifications of the prominent features of a CLD ($l_{MAX}$ and $l_{LPI}$) in a similar manner as does the band broadening in SEC. Furthermore, $l_{MAX}$ as a matter of principle is no ideal substitute for $L_0$, also for number distributions as they result from MALDI−ToF−MS.[4,23]

## Conclusions

A critical reinvestigation and reanalysis of $k_p$ data obtained by means of the PLP−SEC method via a correction procedure by which the majority of shortcomings associated with the replacement of $L_0$ by $l_{LPI}$—as they admittedly were inherent in our previous publications—appears to be eliminated, still favor the existence of a *long* range chain length dependence of $k_p$. Its extent as well as its range even appears to be increased after removing the distortions introduced by the SEC-technique used for CLD analysis. This finding is challenging the alternative view[15] that oversized $k_p(l)$ data of extremely short chains ($l$ at most 5−10) are responsible for this effect exclusively. As a consequence, we suggest that a long-range chain length dependence of $k_p$ should be considered into all advanced modeling procedures of free radical polymerization. This may turn out to be demanding, especially if processes are concerned, which concentrate on the formation of rather short chain polymers although the dependence of $k_p$ on chain length in the short chain and long chain range appear to be well separated and can certainly be traced back to different origins.

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## References and Notes

(1) Kamachi, M.; Yamada, B. in *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, A., Eds.; J. Wiley & Sons: New York **1999**, p II/77ff.

(2) Kaminsky, V.; Buback, M.; Egorov, M. *Macromol. Theory Simul.* **2002**, *11*, 128.

(3) (a) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864 and literature cited therein. (b) Shipp, D. A.; Smith, T. A.; Solomon, D. H.; Moad, G. *Macromol. Rapid Commun.* **1995**, *16*, 837. Heuts, P. A..; Gilbert, R. G.; Radom; L. *Macromolecules* **1995**, *28*, 8771. Zetterlund. P. B.; Busfield, W. K.; Jenkins, I. D. *Macromolecules* **1999**, *32*, 8041.

(4) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689. Olaj, O. F.; Bitai, I. *Angew. Makromol. Chem.* **1987**, *155*, 177.

(5) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O’Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267. Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545.

(6) Aleksandrov, A. P.; Genkin, V. N.; Kitai, M. S.; Smirnova, I. M.; Sokolov, V. V. *Sov. J. Quantum Elektron.* **1977**, *7*, 547.

(7) Kornherr, A.; Zifferer, G.; Olaj, O. F. *Macromol. Theory Simul.* **1999**, *8*, 260.

(8) Buback, M.; Busch, M.; Lämmel, R. A. *Macromol. Theory Simul.* **1996**, *5*, 845.

(9) Sarnecki, J.; Schweer, J. *Macromolecules* **1995**, *28*, 4080.

(10) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913.

(11) Olaj, O. F.; Vana, P.; Zoder, M. *Macromolecules* **2002**, *34*, 1208.

(12) Kornherr, A.; Olaj, O. F.; Schnöll-Bitai, I.; Zifferer, G. *Macromol. Theory Simul.* **2003**, *12*, 332.

(13) Kornherr, A.; Olaj, O. F.; Schnöll-Bitai, I.; Zifferer, G. *Macromolecules* **2003**, *36*, 10021.

(14) Kornherr, A.; Olaj, O. F.; Schnöll-Bitai, I.; Zifferer, G. *Macromol. Theory Simul.* **2004**, *13*, 560.

(15) Willemse, R. X. E.; Staal, B. B.; van Herk, A. M.; Pierik, S. C. J.; Klumperman, B. *Macromolecules* **2003**, *36*, 9797.

(16) Beuermann, S. *Macromolecules* **2002**, *53*, 9300.

(17) Schnöll-Bitai, I. *Macromol. Chem. Phys.* **2002**, *203*, 1754. Schnöll-Bitai, I. *Macromol. Theory Simul.* **2002**, *11*, 770. Schnöll-Bitai, I.; Pfeisinger, C. *Macromol. Chem. Phys.* **2003**, *204*, 384. Schnöll-Bitai, I. *Macromol. Theory Simul.* **2003**, *12*, 111.

(18) Kornherr, A.; Olaj, O. F.; Schnöll-Bitai, I.; Zifferer, G. *Macromol. Theory Simul.* **2003**, *12*, 259.

(19) Schnöll-Bitai, I. *Chromatographia* **2003**, *58*, 375. Schnöll-Bitai, I. *J. Chromatogr. A*, in press.

(20) Olaj, O. F.; Schnöll-Bitai, I. *Eur. Polym. J.* **1989**, *25*, 635.

(21) Axelson, J.; Scrivener, E.; Haddleton, D. M.; Derrick, P J. *Macromolecules* **1996**, *29*, 8875.

(22) Twerenbold, D.; Gerber, D.; Gritti, D.; Gonin, Y.; Netuschill, A.; Rossel, F.; Schenker, D.; Vuilleumier, J.-L. *Proteomics* **2001**, *1*, 66.

(23) Kornherr, A.; Olaj, O. F.; Schnöll-Bitai, I.; Zifferer, G. to be published.

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