# Investigation of the Chain Length Dependence of $k_p$: New Results Obtained with Homogeneous and Heterogeneous Polymerization

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**Summary:** New experimental results were collected for the free radical polymerization of styrene by pulsed laser polymerization in solution or in microemulsion. The location of the point of inflection (on the low molecular weight side) and the maximum of the first peak in the chromatograms (measured by size-exclusion chromatography) was used to extract $k_p$ data. The extent of band broadening was determined with narrow polystyrene standards with an assumed Poisson chain length distribution. For a given experiment both $k_p$ values (obtained via the point of inflection and the maximum) were corrected and thus became identical in most cases. Even after the correction, the effect of chain length dependence persists to a higher chain length.

**Keywords:** gel permeation chromatography; kinetics (polym.); polystyrene; radical polymerization

## Introduction

About six years ago Olaj et al.[1] presented their result that chain propagation in radical polymerization is a chain length dependent (CLD) process. This they deduced from the observation that the rate coefficient determined by the PLP-SEC method (pulsed laser polymerization and subsequent analyses of the chromatograms measured by size-exclusion chromatography) decreased with increasing chain length. Shortly afterwards van Herk and co-worker[2] also presented experimental evidence of this phenomenon. They also included results deduced from chain length distributions measured by matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-ToF). In the latter case they chose the location of the peak maximum as being the proper quantity to yield $k_p$ from the respective chain length $L$ according to[3]

$$k_p = \frac{L}{[M]t_0} \tag{1}$$

$[M]$ signifies the monomer concentration and $t_0$ the time interval between two subsequent laser pulses. When the results for the polymerization of methyl methacrylate at 25 °C were compared it became obvious that the $k_p$ values deduced via the points of inflection showed almost the same general trend whereas the function describing the CLD seemed to be completely different when deduced from the location of the peak maxima from the MALDI-ToF spectra. As a consequence it was concluded by these authors that the observed discrepancies with respect to the considerable chain length dependence at higher chain lengths is a result of the influence of band broadening (BB) on the location of the points of inflection.

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Still, it is not clear whether such a comparison is legitimate because of the following reasons:

a) As a justification for the use of the peak maximum instead of the point of inflection it was claimed that all experiments were carried out in the high termination rate limit.[4] Under such conditions it was shown that the peak maximum yielded the more accurate $k_p$ value. Therefore, this should not only be true for the MALDI-ToF spectra but also for the molecular weight distributions (MWD) determined by SEC.
b) For a comparison the data derived from the points of inflection from the MALDI-ToF spectra and those derived from the maxima from the SEC chromatograms are missing. Such a comparison would have revealed in a more direct way how strong the differences were due to the influence of BB on the location of the inflection point. Although it could, in principle, be speculated whether MALDI measurements are biased by some kind of experimental difficulty it is far more vital to know whether the results obtained with SEC will display a systematic adulteration due to the phenomenon of BB as this is the standard method for the measurement of MWDs. Besides this, it is necessary to be able to determine the extent of BB and furthermore to know how to correct for the deterioriating influence of BB – at least pointwise.

## Phenomenon of BB in SEC

Whenever a uniform sample is measured by SEC a continuous spectrum instead the ideally single line is detected. For such samples it is obvious that BB leads to a broadening of the signal. Synthesis of polymers does not lead to uniform samples but will display a certain chain length or molecular weight distribution in most cases. The narrowest distribution that can be achieved by synthesis alone is a Poisson distribution. Simulations of the effect of BB on the distribution by applying the so called Tung equation[5] revealed that these narrow peaks are also broadened under the influence of BB.

## Determination of BB in SEC

Although the extent of BB could be determined with a variety of methods, a newly developed approach based on the use of samples with Poisson distribution[6,7] was employed. Poisson (number chain length) distributions are characterized by one quantity, namely the location of the peak maximum, $L_{\max}$, which is easily accessible from experiment. Furthermore, it was shown by Chang and coworker[8] that anionically prepared polystyrenes approach Poisson distributions.

The peak width is acquired from chromatograms via the location of the points of inflection ($V_{\text{low}}$, $V_{\text{high}}$). Due to the logarithmic dependence of the molecular weight $M$ on the retention volume $V$ ($\log M = a\text{-}bV$, $a,b$ constants) the difference $V_{\text{low}}\text{-}V_{\text{high}}$ transforms to the ratio of the two corresponding chain lengths according to

$$\begin{aligned}2\sigma_{\text{SEC}} &= V_{\text{low}} - V_{\text{high}}\\ &= \frac{1}{b}\{\log M_{\text{high}} - \log M_{\text{low}}\}\\ &= \frac{1}{b}\log\frac{L_{\text{high}}}{L_{\text{low}}}\end{aligned} \tag{2}$$

When BB can be described by a Gaussian (or exponentially modified Gaussian) function characterized by the variance $\sigma_{\text{BB}}$ (and the exponential decay term $\tau_{\text{BB}}$) then the rearrangement of the experimental peak width $(\sigma^2_{\text{SEC}} = \sigma^2_{\text{BB}} + 0.5\cdot\tau^2_{\text{BB}} + \sigma^2_{\text{Poisson}})$[9] leads to a simple algebraic equation with which the extent of BB can be calculated.

$$\begin{aligned}&\sigma^2_{\text{BB}} + 0.5\cdot\tau^2_{\text{BB}}\\ &\quad = \sigma^2_{\text{SEC}} - \frac{1}{4b^2}\log^2\frac{L_{\max} + L_{\max}^{1/2}}{L_{\max} - L_{\max}^{1/2}}\end{aligned} \tag{3}$$

The second term on the r.h.s. of Equation (3) represents the theoretical peak width of a Poisson distribution.[10]

If we recall the necessary "ingredients" that lead to Poisson distributions, the following prerequisites must be mastered experimentally: First, all propagating chains must be generated at the same instant. Second, any type of chain termination process must be absent during propagation. Third, all active chains must be deactivated at the same time. Besides ideal anionic polymerization there exist several other possibilities to accomplish these conditions. Pulsed laser polymerization in microemulsion can be regarded to fulfill these necessities too, due to the following reasons. The propagating chains are generated during an extremely short laser pulse. The validity of the zero-one condition ensures that the radicals are separated from each other thus inhibiting chain termination events in between two laser pulses. With the arrival of the subsequent laser pulse a certain percentage of the present polymer radicals are terminated within an extremely short period. This means that the accumulated chain length distribution is composed of several Poisson peaks which locations are governed by $k_p[M]t_0$. Overlays of molecular weight distributions[11] of polystyrenes prepared this way and commercially available polystyrene standards revealed an excellent agreement for individual peaks thus demonstrating that both synthetic routes lead to almost identical narrow distributions. Lee and coworker[8] demonstrated that anionically prepared polystyrenes with a peak maximum located between $2 \cdot 10^4$ and $10^6$ gmol$^{-1}$ can be described by Poisson distributions.

## Determined Extent of BB

The investigation of BB carried out with commercially available polystyrene standards as well as polystyrene samples prepared by pulsed laser polymerization in microecmulsion revealed that the extent of BB is not constant over the entire separation range.[11] The function decreases continually from the maximum value at low retention volume. Such a behaviour was already found as early as 1987[12] and later.[13,14] Different column combinations were tested and all results could be described by a somewhat more elaborate van Deemter equation[15]

$$\sigma_{\mathrm{BB}}^2 = \lambda \frac{2d_\mathrm{p}}{l} V^2 + \gamma \frac{2D_\mathrm{m}}{l} \frac{1}{u} V^2 + q \frac{V_0}{l} \times \frac{d_\mathrm{p}^2}{D_\mathrm{s}} u(V - V_0) \qquad (4)$$

$d_\mathrm{p}$ signifies the particle diameter of the separating material, $l$ is the length of the columns, $D_\mathrm{m}$ and $D_\mathrm{s}$ are the respective diffusion coefficients of the dissolved polymer in the mobile (m) and the stationary (s) phase. $V_0$ correspond to the interstitial volume, $u$ is the linear flow velocity and $q$ is equal to 1/30[16]. The diffusion coefficient for polystyrene in THF at 25 °C ($D_\mathrm{m} = KM^\alpha$) can be found in literature.[13]$\lambda$ is a parameter describing the quality of column packing and lies usually in the range of 1 to 10. All experimental result could be described with $\lambda = 1$ and $\gamma = 1$. The diffusion coefficient of the solute in the stationary phase is not known and the ratio of $D_\mathrm{m}$ over $D_\mathrm{s}$ is sometimes described by an exponential function[17] of the form $D_\mathrm{m}/D_\mathrm{s} = \exp\{-\beta(R_\mathrm{s}/R_{1/2}\}$ depending on the aspect ratio of the Stokes radius $R_\mathrm{s}$ over the average pore size $R_{1/2}$. Columns with different pore sizes were combined, but no information exists how to incorporate the influence of different pore sizes. Therefore, the ratio of diffusion coefficients was treated as being constant as an approximation.

## Influence of BB on the Location of the Points of Inflection

BB will always increase the peak width of narrow peaks and therefore it is important to know how strong the location of the points of inflection is shifted due to the influence of BB. Although the extent of BB varied by at least 100% for different column combinations only moderate differences were found with respect to the shift in the location of the points of inflection. The deviations ranged from 2 to 20% when the points of inflection relative to the ideal values for Poisson distributions ($L_{\max} - L_{\max}^{1/2}$) were compared for different column combinations.[18]

In order to understand these results it is necessary to recall that the actual quantity describing the deteriorating effect of BB is not the variance alone but rather the product of the variance and the square of the slope of the calibration curve.[13,19] This dimensionless efficiency parameter is at least one order of magnitude smaller than the variance and the considerable differences reduced to moderate ones. A correction factor *cf* can be constructed to describe the shift[7] of the points of inflection due to BB

$$\log(cf) = \log\frac{L_{\mathrm{corr}}}{L_{\mathrm{exp}}} = b\cdot\mathrm{shift} = b(\sigma_{\mathrm{SEC}} - \sqrt{\sigma_{\mathrm{SEC}}^2 - (\sigma_{\mathrm{BB}}^2 + 0.5\cdot\tau_{\mathrm{BB}})} \tag{5}$$

In order to obtain the true location of the point of inflection on the low molecular weight side the experimental one must be multiplied with this correction factor whereas that at the high molecular weight side must be divided accordingly. The correction factor is highest for uniform samples and Poisson distributions with very high $L_{\max}$ values. For a Poisson distribution with $L_{\max} = 100$ the correction factor is smaller and for distributions centred around still lower values the necessary corrections become even smaller. Thus, evidence is given of the already observed phenomenon that in the case of broad distributions almost no shift in the location of the points of inflection can be observed.

### Correction Procedure for More Accurate $k_p$ Values

With respect to molecular weight distributions obtained when polymers are prepared with pulsed laser polymerization the situation is somewhat more complicated. From

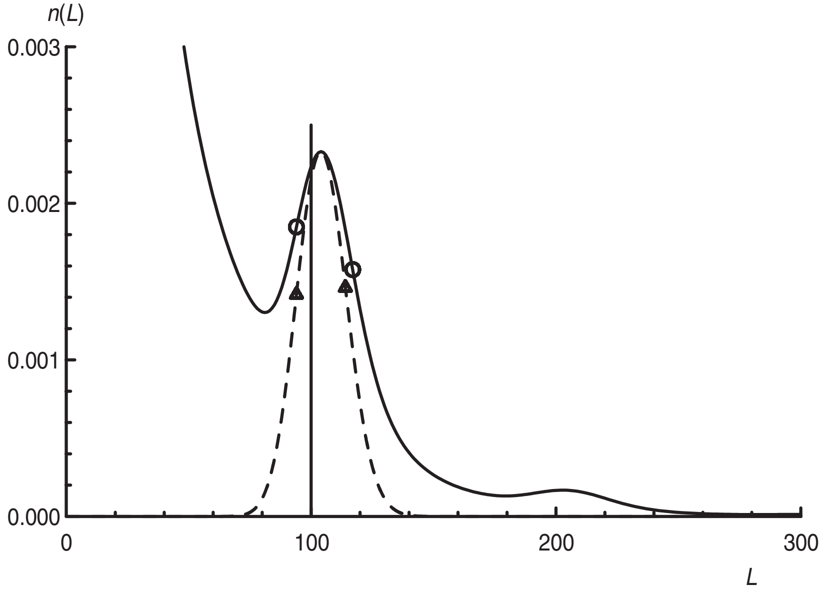

***Figure 1.***
Number chain length distribution, *n(L)*, calculated for homogeneous pulsed laser polymerization and $L_0 = 100$. An ideal Poisson distribution centred at the same $L_{\max}$ value is included and the positions of the points of inflection are presented by circles and triangles.

simulations it can be seen[20] that neither the point of inflection nor the maximum is the ideal value to yield $k_p$ via equation 1 (c.f. Figure 1). Furthermore, the simulations revealed that the peak width is broader than the peak width of an ideal Poisson distribution in most cases[20,21] and that this ''kinetic'' peak width is gouverned by the experimental conditions. Only in the limit of the high termination rate range[4] will the width of the distribution be close to that of a Poisson distribution. The peak width of narrow peaks increases under the influence of BB (not shown in the diagram). Therefore an auxiliary function $X$ is defined as the difference between the experimental peak width and the theoretical one (the peak width of a Poisson distribution broadened by BB):

$$\begin{aligned} X &= \log^2 \frac{L_{\text{high}}}{L_{\text{low}}} - \log^2 \left( \frac{L_{\text{high}}}{L_{\text{low}}} \right)_{\text{theory}} \\ &= \log^2 \frac{L_{\text{high}}}{L_{\text{low}}} - \log^2 \left( \frac{L_{\text{high}}}{L_{\text{low}}} \right)_{\text{Poisson}} - 4\sigma_{\text{BB}}^2 \end{aligned} \tag{6}$$

From several number chain length distributions simulated for pulsed laser polymerization for a great variety of experimental parameters[21] which were converted to chromatographic dimensions and subsequently submitted to the influence of BB by applying the Tung equation[5] correction functions were deduced. The comparison of the input values for the point of inflection and the maximum lead to the following correction functions:

$$f_X^{\text{LPI}} = \frac{L_0}{L_{\text{LPI}}} = (I_I + S_I\sigma^2) - (I_S + S_S\sigma^2)X \tag{7a}$$

$$f_X^{\text{MAX}} = \frac{L_0}{L_{\text{MAX}}} = (I_I + S_I\sigma^2) - (I_S + S_S\sigma^2)X \tag{7b}$$

where $I$ and $S$ signify the respective intercepts and slopes. It was already demonstrated that without a correction the under estimation of $k_p$ (when deduced from the point of inflection) can be as high as 15% whereas the maximum can lead to an over estimation of almost 40%. Whenever these corrections are applied the true $L_0$ value should be obtained by both approaches with a higher accuracy. Thus, the question of whether the maximum or the point of inflection is the better means to obtain correct $k_p$ values is of no importance as the correction should lead to identical values when carried out properly. The extent of BB is an essential quantity and must be known or determined beforehand in order to be able to apply this correction.

## Experimental Part

### Pulsed Laser Polymerization in Microemulsion

Polymerization was either carried out in solution (50 wt.-% toluene and styrene, each) or in microemulstion. In the latter case the polymerization mixture was prepared according to the recipe of Gan and coworker.[22] The oil phase consisted again of 50 wt.-% toluene and styrene, each. For all experiments 2,2′-azoisobutyronitrile (AIBN) was used as a photoinitiator at a concentration of $5 \cdot 10^{-3}$ moll$^{-1}$ for the polymerization in solution and $44 \cdot 10^{-3}$ moll$^{-1}$ with respect to the oil phase. The polymerization mixture was purged with Argon (15 min) prior to polymerization. For the intermittant illumination a Nd:Yag laser (Quanta Ray GCR-130-20) was used at different pulse frequencies. All polymerizations were carried out at $T = 25\,^\circ$C to low conversions only (in order to avoid phase separation). Immediately after irradiation all radicals were deactivated by injecting a solution of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) in toluene. The polymers were precipitated in pure methanol and filtered. Detergent was removed by carefully washing with water and methanol several times.

### Size-exclusion Chromatography

A combination of four SDV columns ($10^6$, $10^5$, $10^4$, $10^3$; 8 mm × 300 mm, particle diameter = 10 μ) from Polymer Standard Service (PSS) were used. THF was the solvent for the polymer and the eluent at a flow rate of 1 ml min$^{-1}$. A differential refractive index detector (Waters 2412) was employed. With the aid of narrow polystyrene standards from PSS and scientific products a third order polynomial calibration curve was constructed. The molar mass distributions were exported and numerical differentiation was carried out with a home made software[23] in order to determine the location of the points of inflection and the peak maximum. From the analysis of the polymer standards the extent of BB was determined following the procedure outlined in the preceding paragraph.

## Results and Discussion

With respect to the polymerization in microemulsion there is the question about the actual monomer concentration which seems to be smaller than the nominal one.[22] For a comparison of the $k_p$ values obtained from homogeneous and heterogeneous polymerization it would be necessary to know this quantity with certainty. As this is not the case comparison of the natural logarithm of $k_p[M]$ values for the two different systems is shown in Figure 2 as the concentration will only contribute additively in this case and the results are shifted along the ordinate. Thus the chain length dependence of the $k_p$ values can not only be compared directly for the two polymerization systems but can also be compared with the data published by Willemse et al.[2]

The filled diamonds (triangles) represent the results for the polymerization in microemulsion (solution) as deduced from the location of the point of inflection on the low molecular weight side; the full squares (inverted triangles) represent the data obtained from the peak maximum. All four data sets show the same general trend of a chain length dependence persisting to higher chain lengths as was already shown by Olaj et al.[1,24]

In order to make sure that BB can be excluded as a possible source for discre-

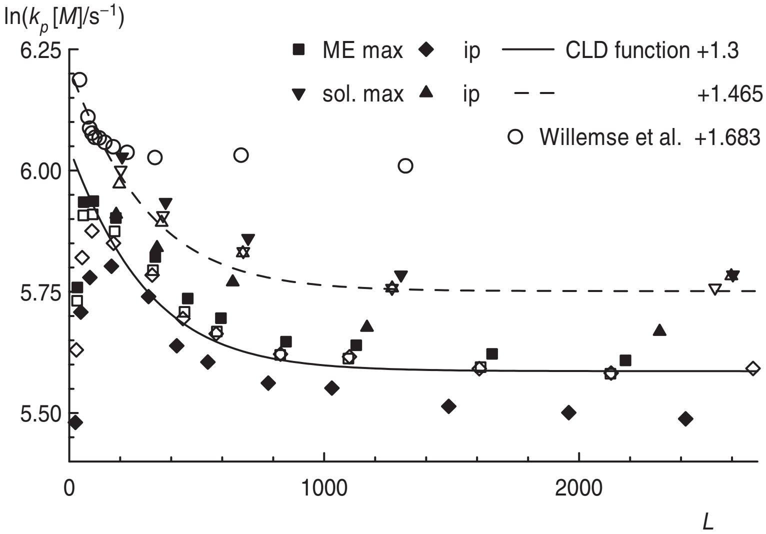

*Figure 2.*
Comparison of uncorrected $k_p$ values (full symbols) for the polymerization a) in microemulsion: diamonds (inflection points, ip) and squares (maximum, max) and b) in solution: triangles (ip) and inverted triangles (max). The corresponding open symbols represent the results after application of the correction (Equations (7a) and (7b)). The CLD function calculated according to Equation (8) is included as full and broken curve, respectively, which are only shifted by the constant value as indicated.

pancies the correction procedure presented above was applied to the data sets. The investigated peak widths (determined via the points of inflection) were very close or identical to those of the corresponding Poisson distributions broadened by BB. Therefore, the auxiliary function was zero and the second term in the Equations (7a) and (7b) did not contribute to the correction; the values for the slope $S$ and the intercept $I$ were taken from literature.[20] The corrected values are depicted as open quadrangles (triangles) in Figure 2. The correction lead to identical values deduced from the maximum and the points of inflection and did not change the type of the CLD. The corrected data can be described by the exponential model

$$\ln k_{\mathrm{p}}(L) = \ln kLk_{\mathrm{p}} - \ln\left\{\ln\left[1 + \frac{k_{\mathrm{p}}(\infty)}{k_p(0)}(e^{kL} - 1)\right]\right\} \quad (8)$$

with the coefficients as given in reference [21]. In all, the results from heterogeneous (full curve) and homogeneous (broken curve) polymerization can be described by one function which is merely shifted along the ordinate as indicated in the diagram.

For comparison the data deduced from the peak maxima of MALDI spectra[2] (open circles) were converted to 25 °C by applying the Arrhenius equation (parameters from ref.[2]]) and were shifted by a constant value so that the high frequency values lay on the broken curve. Thus, a completely different CLD behaviour becomes obvious as the effect levels off at a chain length of approximately 300 where it converges towards a constant value. When the data obtained via MALDI is compared with that deduced by the same group from SEC measurements[2] a similar CLD behaviour becomes obvious which clearly does not support the idea that BB can be made responsible for the observed differences.

Agreement with the Willemse data[2] is only given at higher frequencies whereas the decrease in the $k_{\mathrm{p}}$ values at lower frequences was less pronounced. The maximum difference corresponds to about 0.3 on the logarithmic scale which means that the peak maxima are about 40% higher in comparison.[21] This is of a comparable dimension as the error introduced by (wrongly) using the location of the peak maximum in the low termination rate limit.[25] This leads to the question whether polymerization was really carried out in the high termination rate limit in all cases as was claimed by the authors. Usually, laser intensities decrease dramatically with increasing pulse separation times what would lead to the generation of lower concentrations of initiating radicals. Unfortunately, information about laser intensities are missing in most publications and one is thus left to decide what limit applies without an impartial criterion.

## Conclusion

Homogeneous and heterogeneous pulsed laser polymerization of styrene was carried out at 25 °C. For the extraction of the $k_{\mathrm{p}}$ values as a function of the chain length from measured SEC curves it was necessary to determine the extent of BB. The analyses of narrow Poisson-like polystyrene standards revealed a non constant extent of BB over the complete separation range which could be described by a somewhat more elaborate van Deemter equation.[11,13,14] The shift of the points of inflection and as a consequence the introduced error correlates directly to the extent of BB.[18]

The application of the correction procedure[21] lead to identical results when both options (point of inflection and maximum) were used. The type of the chain length dependence deduced from polymers prepared by homogeneous and heterogeneous polymerization was the same which is demonstrated in Figure 2 as they simply differ by a constant term. The persistence of the chain length dependence to higher degrees of polymerization is not in agreement with the results from

Willemse et al.[2] and deviates also from theoretical expectations.[26] This leads to the ultimate questions: a) What is the reason for the differences of the deduced $k_p$ values? b) Can we influence the experimental parameters in such a way to switch from one experimental result to the other? And c) Are there only two distinct possibilities – like switching from one state to the other – or is it possible to change continuously from one type of functionality to the other?

The collection of data and critical evaluation of possible influences of parameters on the CLD (as was carried out by Heuts et al.[26]) might help to elucidate the current question of the true nature of chain length dependence of the rate constant of propagation in free radical polymerization. Therefore, the investigation of the polymerization behaviour of monomers other than styrene and methyl methacrylate is necessary[27] and the use of the correction procedures[20,21] should eliminate the error introduced by the effect of BB. Thus, comparison of data obtained from either different research groups and/or with the aid of different techniques[2,28] (MALDI, SEC) should be better feasible.

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