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Pseudostationary Polymerization: Improving the Determination of the Rate Constant of Propagation

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Summary: Pulsed-laser initiated polymerization (PLP) leads to chain length distributions with characteristic extrapeaks. The low molecular weight side points of inflection L_{LPI} are located near to (multiples) of a specific chain length L_0 which is equal to the product of pulse separation t_0 and propagation frequency $k_p[M]$, i.e. rate constant of propagation k_p times monomer concentration $[M]$, allowing a direct determination of k_p. However, Poissonian broadening inherent in the polymerization process as well as Gaussian broadening due to axial dispersion caused by the size exclusion chromatographic (SEC) device leads to a shift of L_{LPI} as compared to L_0 – its extent depending on the experimental parameters chosen – which in turn causes an error up to 10–20% in the rate constants evaluated. Fortunately, comparison of the experimental peak width with some sort of theoretical peak width yields several types of correction factors and furthermore master-correction functions which are able to reduce the remaining error on average by at least a factor of 10.

Keywords: axial dispersion; laser-induced polymers; propagation rate constant; radical polymerization; size exclusion chromatography

Introduction

Polymerization induced by pulsed-laser initiation (PLP) with subsequent analysis of the chain length distribution (CLD) by size exclusion chromatography (SEC) of the polymer formed directly yields the propagation rate constant k_p from the position of the "extra-peaks" appearing in the CLD which arise because of the correlation between the initiation of radical chains (within the narrow time interval of the laser flash) and their termination (by the increased concentration of radicals produced in subsequent flashes). Theoretical distribution curves which neglect the fluctuation of propagation (assuming a strict proportionality between chain length L and growth time t of a radical chain) exhibit discontinuities in form of edges at the positions $n \cdot L_0$ ($n = 1,2,3,\ldots$) with $L_0 = k_p[M]t_0$ ($[M]$ being the monomer concentration and

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t_0 the time interval between two successive laser pulses). Using this relation between t_0 and L_0 the rate constant of propagation could be immediately calculated from a single PLP chain length distribution with utmost accuracy. However, the stochastic character of the propagation process replaces these edges by peaks – consisting of a superposition of Poissonian peaks (Poissonian broadening) – whose points of inflection on the low molecular weight side (LPI) are located near to the positions of the former edges, i.e. $L_{\mathrm{LPI}}/n \approx L_0$, see Figure 1.

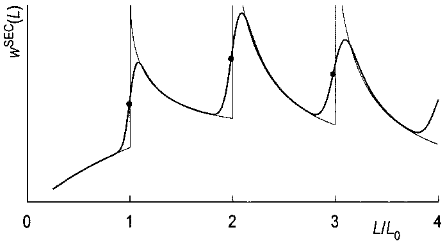

Figure 1. Theoretical SEC-distribution vs L/L_0 calculated assuming strict correlation between time t and degree of polymerization L (thin line) and applying in situ Poissonian broadening[6] (thick line) for termination by disproportionation assuming a moderate chain length dependence of the termination rate coefficient $k_t^{(x,y)}=k_t\cdot(xy)^{-0.08}$ between radicals of length x and y using parameters $L_0 = 400$ and $C = k_t\cdot\rho\cdot t_0 = 2.5$ (ρ = primary radical concentration).

Introduced 17 years ago,[1] the method was adopted by research groups all over the world within few years and was recommended by the IUPAC as a standard method of determining k_p[2,3]; the overwhelming progress in accuracy and reliability was recently impressively demonstrated by Gilbert et al.[4] Nevertheless, there are some problems remaining concerning the evaluation of L_0. Based on theoretically evaluated or numerically calculated chain length distributions it has been shown that L_{LPI} indeed is a good representative for L_0 for the majority of experimental conditions;[1,5,6] only in the so called high termination limit with high laser intensities and/or sensitizer concentrations, i.e. large ρ (corresponding to large C and small L_0 in the simulation) the position of the maximum L_{MAX} appears to be the more favorable approximation.[7] However, analyzing chain-length distributions experimentally, a further source of inaccuracy arises: During the development of the distribution (fractionation process) within the size exclusion chromatographic device (Gaussian) broadening occurs due to axial dispersion which causes a further shift of L_{LPI} (and simultaneously of the position of the maximum L_{MAX} as well as the position of the point of inflection on the high molecular weight side L_{HPI}). This is demonstrated in Figure 2 subjecting a theoretical (more precisely, numerically calculated) distribution curve to Gaussian broadening[8,9] (based on the Tung[10] equation) simulating small ($\sigma = 0.025$), moderate ($\sigma = 0.050$) and large ($\sigma = 0.075$) axial dispersion. A description of the calculation procedure is omitted here; for details, e.g., see.[9] It should be noted that experimental SEC-distributions are based on elution volumes which are connected with the logarithm of respective molar masses thus resulting in $w^{\mathrm{SEC}}(L)$ vs $\lg(L)$ diagrams. As in numerical treatements the primary result is the number distribution (on a linear scale) we prefer the $w^{\mathrm{SEC}}(L)$ vs L scale although Gaussian broadening is clearly performed on the logarithmic scale in order to portray axial dispersion inside the SEC column.

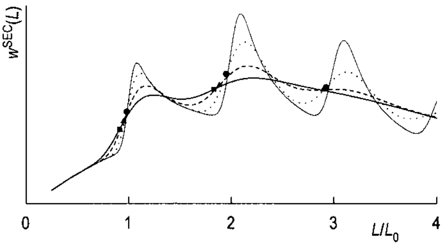

Figure 2. Theoretical SEC-distribution vs L/L_0 calculated for various extents of axial dispersion, LPI marked by a symbol: $\sigma = 0.025$ (dotted line, circle), $\sigma = 0.05$ (broken line, triangle) and $\sigma = 0.075$ (full line, square); for comparison the curve for $\sigma = 0$ (thin line, identical to the bold curve in Figure 1) is shown, too. Parameters as in Figure 1.

The further discussion is restricted to the first peak only: Generally, for $\sigma = 0$ $L_{\mathrm{LPI}}/L_0 < 1$ and the deviation of L_{LPI}/L_0 from unity is the smaller the smaller is C and the larger is L_0 as long as the extrapeak in the SEC-distribution is well defined. For ill-defined peaks exhibiting no maximum L_{LPI}/L_0 occasionally may exceed unity (low termination limit with small C and L_0); this latter effect is more pronounced for termination by combination. With increasing axial dispersion, i.e. with increasing σ in the simulation, the deviation from unity is enlarged, yielding to $L_{\mathrm{LPI}}/L_0 = 0.8$ to 0.9 for most samples in case of σ=0.075. In all, the accuracy of the rate constant of propagation calculated from L_{LPI} slightly depends on the experimental condition chosen and strongly on the extent of axial dispersion. Although this fact is well known since several years[8] no method of applying *quantitative* corrections to the quantities to be used as substitutes for L_0, i.e. L_{LPI} or L_{MAX}, respectively, was available. Thus, we set out to develop suitable corrections which may be derived from experimentally obtained CLDs themselves (or at least from some parameters extracted): Based on simulated CLDs covering a wide range of reasonable experimental conditions and considering both types of broadening

(Poissonian due to the fluctuation of propagation and Gaussian due to axial dispersion) the correction factors L_0/L_{LPI} (and L_0/L_{MAX}) were shown to be unique functions of several quantities derived from experimental and theoretical peak broadness for a given σ value[9]. As a next step masterfunctions were developed which allow the calculation of the correction factors L_0/L_{LPI} and L_0/L_{MAX} for any arbitrary axial dispersion[11]. In the present communication a further master-correction function (based on an extended set of data given in[9]) which is different from those given in[11] is proposed.

Master-correction-function for improving the evaluation of k_p

The definition of the (relative) peak width[12] as the ratio of the chain lengths characteristic of the points of inflection on the high, L_{HPI}, and low, L_{LPI}, molecular weight side of each peak is the key to the success of the method proposed:

$$\delta = \frac{L_{\mathrm{HPI}}}{L_{\mathrm{LPI}}}$$

From an experimental distribution the experimental peak width δ_{E} is obtained which may be compared to the peak width of some standard, i.e. the peak width δ_{T} of a Gaussian broadened Poissonian peak exhibiting its maximum at the same position L_{MAX} as the experimentally obtained peak under consideration.

As δ is directly related to the chromatographically determined width, $2\sigma_{\mathrm{SEC}}$, according to

$$2\sigma_{\mathrm{SEC}} = V_{\mathrm{e,low}} - V_{\mathrm{e,high}} = \frac{1}{k}\{\lg M_{\mathrm{HPI}} - \lg M_{\mathrm{LPI}}\} = \frac{1}{k}\lg\frac{L_{\mathrm{HPI}}}{L_{\mathrm{LPI}}} = \frac{1}{k}\lg\delta$$

(k representing the slope of a linear calibration curve $\lg(M) = a - kV_{\mathrm{e}}$, with V_e being the elution volume) the influence of axial dispersion on the peak width of a Poissonian peak

$$\delta_{\mathrm{P}} \approx \frac{L_{\mathrm{MAX}} + \sqrt{L_{\mathrm{MAX}}}}{L_{\mathrm{MAX}} - \sqrt{L_{\mathrm{MAX}}}}$$

directly follows from the relation

$$\lg^2\delta_{\mathrm{T}} = \lg^2\delta_{\mathrm{P}} + 4\sigma^2$$

with $\sigma \equiv k\cdot\sigma_{\mathrm{ad}}$ obtained assuming additivity $\sigma_{\mathrm{SEC}}^2 = \sigma_{\mathrm{P}}^2 + \sigma_{\mathrm{ad}}^2$ of the intrinsic variance of the peak σ_{P}^2 and contribution from axial dispersion σ_{ad}^2. What follows is a well defined correlation between the ratio L_{LPI}/L_0 (or correction factors L_0/L_{LPI}, respectively) and several combinations of δ_{E} and δ_{T}, e.g. $X \equiv \lg^2\delta_{\mathrm{E}} - \lg^2\delta_{\mathrm{T}}$.

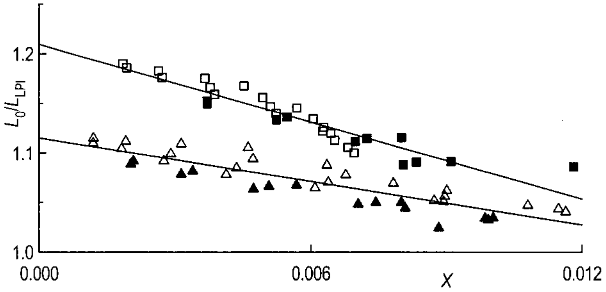

Figure 3. Correction factors L_0/L_{LPI} versus $X \equiv \lg^2\delta_E - \lg^2\delta_T$ for $\sigma = 0.05$ (triangles) and $\sigma = 0.075$ (squares) calculated for $50 \le L_0 \le 800$, $0.3 < C \le L_0/5$; termination by disproportionation (open symbols) and termination by combination (closed symbols).

Fitting the data for each σ value to a straight line immediately yields a correction function for this special axial dispersion. Analyzing the dependence of intercepts and slopes on σ results in a (linear) master equation[12] with slope and intercept itself being functions of σ. Another route is to shift the data points along the abscissa so that the (original) intercept of a given line (e.g. $\sigma = 0.05$) is located on the regression line for the next σ value (i.e. $\sigma = 0.075$ in this example), the X value where the regression line through $\sigma = 0$ data (not shown in Figure 3) passes $L_0/L_{LPI} = 1$ serving as the new zero of the abscissa. Fitting the transformed data to a polynomial with a horizontal tangent in (0/1) finally yields a master-correction function

$$f^{corr}(X,\sigma) = 1 + 260 \cdot \left[X - (0.008 + 0.28\sigma)\right]^2$$

depicted as full line in Figure 4.

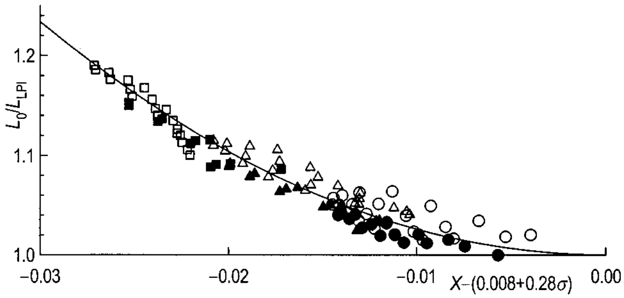

Figure 4. Correction factors L_0/L_{LPI} versus shifted abscissa $X-(0.008+0.28\sigma)$ for $\sigma = 0.025$ (circles), $\sigma = 0.05$ (triangles) and $\sigma = 0.075$ (squares) calculated for $50 \le L_0 \le 800$, $0.3 < C \le L_0/5$; termination by disproportionation (open symbols) and termination by combination (closed symbols) and master-correction-function (full line).

Application of this master-correction-function cuts down the remaining error in L_0 to less than 1% on average, the maximum error not exceeding 3% in the worst case. This is demonstrated in Figure 5 for intermediate and large axial dispersion.

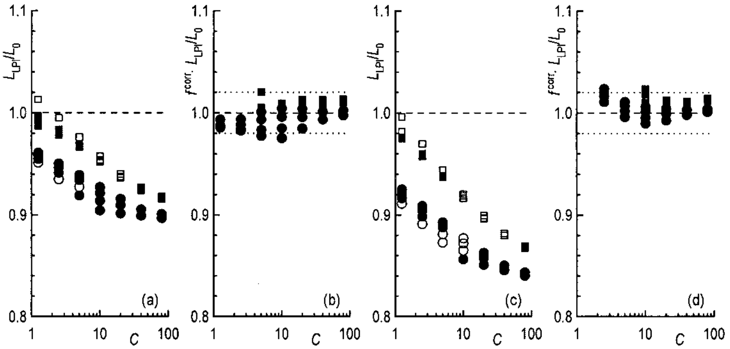

Figure 5. Application of the correction function on raw data $\sigma = 0.05$ (a) and $\sigma = 0.075$ (c) yields improved values (b) and (d), respectively. Termination by disproportionation (circles) and combination (squares). Open symbols represent ill-defined peaks without a maximum.

Conclusion

The procedure outlined above (together with alternative correction functions given in[11]) leads to a substantial improvement of the theoretical basis of the evaluation of the quantity L_0 necessary for the determination of k_p by means of the PLP-SEC method.

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