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Masterfunctions Providing a Sound Theoretical Basis for the Extraction of Accurate k_p Data from PLP−SEC Chain-Length Distributions Exhibiting Poissonian and Gaussian Broadening

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ABSTRACT: The positions of the maxima $l_{\max}$ of the first "extra peak" that appears in chain-length distributions (CLDs) evaluated by the pulsed laser polymerization−size exclusion chromatography (PLP−SEC) method, and the positions of the points of inflection on the low-molecular-weight side of this peak (l_{LPI}), are known to be approximate, but more-or-less inaccurate, representatives of the characteristic chain length (L_0) needed for the determination of the rate constant of chain propagation (k_p), according to the relation $k_p = L_0/([\mathrm{M}]t_0)$, where [M] is the monomer concentration and t_0 is the separation of two successive laser pulses. The deviation of l_{LPI} and l_{MAX} from L_0 depends on the reaction conditions and, above all, the extent of the axial dispersion ($\sigma_{\mathrm{ad},k}$) caused by the size exclusion chromatography (SEC) device. On the basis of simulated CLDs that cover a wide range of reasonable experimental conditions, considering Poissonian (due to the fluctuation of propagation) and Gaussian (due to axial dispersion) broadening, the correction factors L_0/l_{LPI} and L_0/l_{MAX} first were shown to be unique functions of a quantity that can be used to compare the experimental and theoretical peak broadness for each $\sigma_{\mathrm{ad},k}$ value ($\sigma_{\mathrm{ad},k} =$ 0.00, 0.025, 0.050, 0.075). As a next step, masterfunctions were developed, which allow calculation of the correction factors L_0/l_{LPI} and L_0/l_{MAX} for any arbitrary $\sigma_{\mathrm{ad},k}$ value. These factors are able to reduce the remaining error in L_0 to <1%, on average, if L_0/l_{LPI} is used and the mode of termination (disproportionation or combination) is known. However, in the other cases (L_0/l_{MAX}, and/or lacking knowledge about the mode of termination), the error that remains is only slightly larger. In one case, a masterfunction could be developed (for L_0/l_{MAX}, in this case) in which $\sigma_{\mathrm{ad},k}$ does not enter as a parameter explicitly. Because of this feature, it is this masterfunction that is probably best-suited for an a posteriori improvement of older k_p data, although the remaining error here is somewhat larger (≈2%).

Introduction

Ever since the basic kinetic scheme of radical polymerization has been established, it has been a desire of many polymer kineticists to be in command of reliable data on the *individual* rate constants of propagation and termination (k_p and k_t, respectively). The problem is that, from stationary polymerization, the two constants emerge in the combination k_p^2/k_t, which can be separated into its components only by evaluating some other combination, e.g., k_p/k_t from instationary or classical pseudo-stationary (rotating sector) experiments, or what would be preferable, by obtaining one of the two individual constants directly. Unfortunately, however, the first approach, apart from the fact that *indirect* methods are always subject to larger errors, suffers from the comparatively low precision of these types of pseudo-stationary experiments, whereas the second approach failed because of a lack of suitable methods of direct determination of one of the two quantities, at least until the late 1980s. Things are best documented by the entries into the *Polymer Handbook*,[1] which most impressively reveals the large scatter of the k_p and k_t data, even for well-behaved and much-investigated monomers such as styrene and methyl methacrylate. The situation was drastically improved with the invention of pulsed laser polymerization (PLP), which is based on the photoinitiated preparation of polymer samples by periodic laser pulses, followed by an analysis of the chain-length distribution (CLD) by means of size exclusion chromatography (SEC).[2,3] This method makes use of the correlation between time t and chain length l, according to the relation

$$l = k_p[\mathrm{M}]t \tag{1}$$

with [M] being the monomer concentration. For periodic laser pulses separated by a constant time t_0, this transforms to

$$L_0 = k_p[\mathrm{M}]t_0 \tag{2}$$

where L_0 is a characteristic chain length that corresponds to a (mean) radical lifetime of t_0. Actually, L_0 can be determined from the CLD: a radical that has been initiated by the previous pulse and has escaped termination up to time t_0 is suddenly opposed to a much larger radical concentration when the next pulse arrives. This means a drastic increase in termination probability, which causes a sudden increase in the CLD for chain lengths close to L_0. If the correlation between t and l were perfect, the CLD (as a number distribution, $x(l)$, the CLD would appear similar to curve a in Figure 1a in this case) would exhibit an infinitely steep increase (a discontinuity) exactly at L_0. Because of the genuine fluctuation of the propagation process, however, every individual chain length in curve a is spread according to a Poissonian distribution, which leads to the picture represented by curve b of Figure 1a. It was shown already in our very first paper[2] on this subject that, for most common experimental conditions, the position

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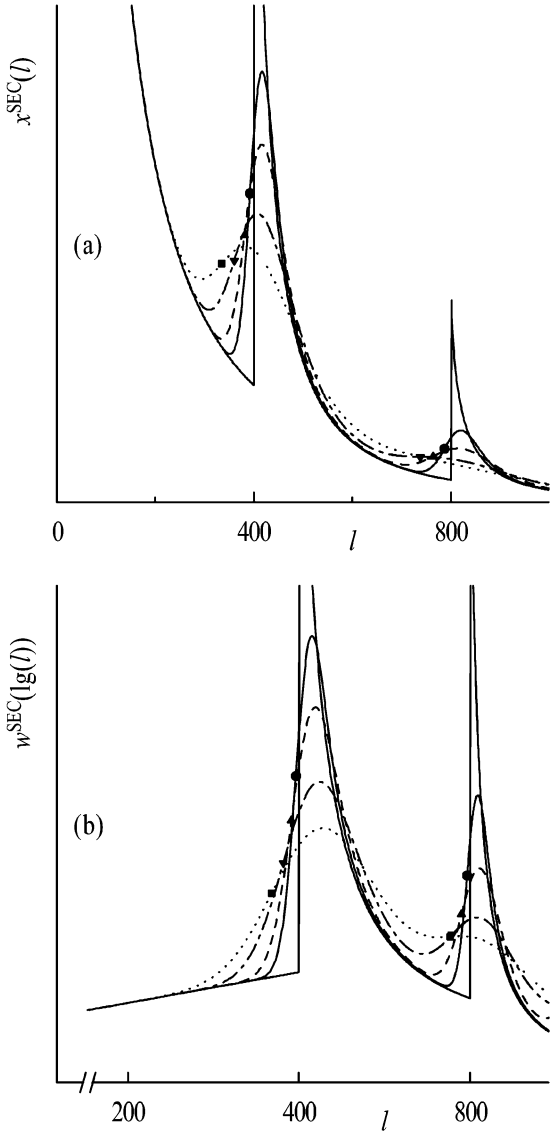

Figure 1. (a) Number distributions ($x^{SEC}(l)$) and (b) hyper mass distributions ($w^{SEC}(\log l)$), calculated for $L_0 = 400$, $C = 10$, and $b = 0.16$ for termination by disproportionation, assuming a strict coupling of time and the degree of polymerization (curves a, full line with edges), regarding Poissonian broadening due to fluctuation of propagation (curves b, smooth full line) and concerning both Poissonian and Gaussian broadening using axial dispersion parameters of $\sigma_{ad,k} = 0.025$ (curves c, broken line), $\sigma_{ad,k} = 0.050$ (curves d, dot−dash line) and $\sigma_{ad,k} = 0.075$ (curves e, dotted line). Points of inflection on the low-molecular-weight side are indicated by symbols.

l_{LPI} of the point of inflection (LPI) that precedes (i.e., on the low-molecular-weight side of) the maximum is a good representative for L_0; this choice is definitely better than that of the position of the maximum l_{MAX}, although it also has a slight amount of error. Within a few years, the method was adopted by research groups throughout the world and was recommended by the International Union of Pure and Applied Chemistry (IUPAC) as a standard method of determining k_p.[4,5] Although the overwhelming progress in accuracy and reliability was recently, and impressively, demonstrated by Gilbert et al.,[6] there are some problems that remain, in regard to the evaluation of L_0. Sarnecki and Schweer[7] argued, from an analysis of the theoretical CLD given by Aleksandrov et al.,[8] that, for high concentrations (ρ) of radicals formed per pulse (i.e., in the so-called high termination rate limit), both l_{LPI} and l_{MAX}, the latter of which normally overestimates L_0 appreciably, decrease to much lower chain lengths, so that, finally, l_{MAX} would be the more appropriate substitute for L_0, with l_{LPI} being largely in error. In reality, however, the CLD is further spread by the axial dispersion in the SEC device that is normally used for the analysis of the CLD (see curves c, d, and e in Figure 1), giving the situation for increasing extents of axial dispersion, which is characterized by the parameter $\sigma_{ad,k}$ ($\sigma_{ad,k} = 0.025$, 0.050, and 0.075, respectively, with curve b formally corresponding to $\sigma_{ad,k} = 0$). In practice, $\sigma_{ad,k}$ depends on the type and number of columns used and is usually in the range of $0.04 \leq \sigma_{ad,k} \leq 0.07$. Figure 1b (curves a−e) represents the CLD in the form of a weight distribution, plotted on a logarithmic l scale, $w^{SEC}(\log l)$, as it would result from an SEC device with mass-sensitive detection, under the same conditions as those for Figure 1a. Actually, the positions of the points of inflection (on the low-molecular-weight side of the maximum), l_{LPI}, as well as the positions of the maxima, l_{MAX}, exhibit a complicated pattern, depending on the extent of axial dispersion and the reaction conditions (t_0 and especially the quantity ρ), which make it impossible to fully utilize the potential of the method if small differences of k_p are to be detected, as is the case, for instance, when the comparative influence of solvents on k_p is examined[9−13] or the chain-length independence of k_p is questioned.[14,15] Some years ago, Buback et al.[16] already conducted an investigation of CLDs simulated using the Predici software, in which they confirmed that l_{LPI} is the better choice for moderate conditions of initiation whereas l_{MAX} is better-suited when very high laser intensities and/or sensitizer concentrations are applied. In addition, Schweer and Sarnecki[17] (and, somewhat later, Buback et al.[16]) were the first to note the influence that the axial dispersion has on the experimentally determined quantities l_{LPI} and l_{MAX}. Beuermann, in a very recent communication[18]—again, based on CLDs calculated by Predici—made valuable comments on the experimental conditions to be chosen when the chain-length dependence of k_p is under investigation. In neither case, however, was an explicit recommendation given (or, equivalently, a suitable method proposed) to apply *quantitative* corrections to the quantities to be used as substitutes for L_0 (l_{LPI} and l_{MAX}). To be practical, these corrections certainly had to be derived from the experimentally obtained CLDs themselves (or at least from some extracted parameters). This seems to be an insurmountable problem initially, because of the following question: where should the desired information be hidden in a CLD of the type shown in, for example, curves b−e in Figure 1b? Surprisingly, however, on the basis of some very careful examinations of peak widths in simulated CLDs that considered genuine Poissonian broadening as well as Gaussian broadening caused by axial dispersion, one of us[19] was able to detect some correlations between the peak widths and the shifts of l_{LPI} and l_{MAX}, relative to L_0. In continuation, supported by the assumption of a Pythagorean additivity of individual variances s^2 that sum up to a total variance, we not only succeeded in devising a method of determining the extent of axial dispersion $\sigma^2_{ad,k}$ (by subtracting the Poissonian variance from the total variance), leaving a measure of the residual variance caused by the SEC device,[20] but we also were able to detect some correlations between the properties of the CLDs and the shifts of the points of inflection and maxima, relative to the theoretical value of L_0, at least for the first peak, which is produced by radicals with a mean life of approximately $1 \times t_0$. Actually, the asymmetric form of the primary peak, shown in curve a of Figure 1a and 1b, is responsible for all the problems under discussion, of course. Provided that the average chain lengths were sufficiently high ($l \geq 50$), neither the genuine Poissonian broadening nor the Gaussian SEC broadening would produce a significant shift of the position of the maximum. Because of the specific (asymmetric) form of the "extra peaks" in the fully undistorted distribution (curve a in Figure 1a and 1b), where l_{LPI} and l_{MAX} formally coincide, l_{LPI} is induced to shift to the left and l_{MAX} to the right until, for extreme conditions, this shift of l_{MAX} is offset again. Thus, in a very recent paper,[21] we have tried to correlate all these shifts (falsifications) of l_{LPI} and l_{MAX}, relative to L_0, with the *residual* variance of the *original* extra peak in a specific case. Certainly, these shifts depend on the extent of the axial dispersion. The purpose of this communication is to generalize these ideas for variable values of the axial dispersion, thus enabling any experimental worker to correct his l_{LPI} and l_{MAX} values, and to provide an improved theoretical basis for the evaluation of L_0 and, accordingly, k_p also. This seems to be absolutely desirable, because, according to the calculations that were made by Buback et al.[16] for $\sigma_{\mathrm{ad},k} = 0.075$, the true values of L_0 (when identified with l_{LPI}) might be in error by approximately (−)20% and even by approximately (+)-40% when derived from l_{MAX} under the most unfavorable conditions.

Definitions

The (relative) peak width is defined in this paper as the ratio of the chain lengths characteristic of the points of inflection on the high- and low-molecular-weight side (l_{HPI} and l_{LPI}, respectively)[19−24] of each peak (always >1):

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

It is directly related to the chromatographically determined width ($2\sigma_{\mathrm{SEC}}$), according to the relation

$$\begin{aligned} 2\sigma_{\mathrm{SEC}} &= V_{\mathrm{e,low}} - V_{\mathrm{e,high}} \\ &= \frac{1}{k}(\log M_{\mathrm{HPI}} - \log M_{\mathrm{LPI}}) \\ &= \frac{1}{k}\log\left(\frac{l_{\mathrm{HPI}}}{l_{\mathrm{LPI}}}\right) \\ &= \frac{1}{k}\log \delta \end{aligned} \tag{4}$$

where k represents the slope of the linear calibration curve $\log M = a - kV_e$, with V_e being the elution volume. This standard deviation is composed of the pristine peak width (σ_P) and the contribution from axial dispersion (σ_{ad}). For narrow peaks (Poissonian peaks), both variances contribute in an additive way to the experimental peak variance:

$$\sigma_{\mathrm{SEC}}^2 = {\sigma_P}^2 + \sigma_{\mathrm{ad}}^2 \tag{5}$$

As a consequence, the theoretical relative peak width, taking into account the influence of axial dispersion, can be expressed as

$$(\log \delta_T)^2 = (\log \delta_P)^2 + 4k^2\sigma_{\mathrm{ad}}^2 \tag{6}$$

with (for Poisson distributions)

$$\delta_P = \frac{l_{\mathrm{MAX}} + \sqrt{l_{\mathrm{MAX}}}}{l_{\mathrm{MAX}} - \sqrt{l_{\mathrm{MAX}}}} \tag{7}$$

and

$$\sigma_{\mathrm{ad},k} \equiv k\sigma_{\mathrm{ad}} \tag{8}$$

where $\sigma_{\mathrm{ad},k}$ is the quantity, in practical use, describing the extent of axial dispersion that is composed of the standard deviation σ_{ad} of the Gaussian axial dispersion function and the slope k of the linear calibration curve.

Simulation Procedure

A lot of different CLDs, characterized by the system-dependent quantities k_p, [M], k_t, ρ (the concentration of radicals produced in each pulse), and t_0 (all of which enter the simulation in the form of dimensionless parameters: $C = k_t\rho t_0$ and $L_0 = k_p[\mathrm{M}]t_0$), were calculated for termination by disproportionation (D) as well as for termination by combination (C) for a broad range of parameters ($50 \leq L_0 \leq 800$, $1.25 \leq C \leq L_0/5$). The actual computation follows a procedure that has already been described in the work of Olaj et al.,[25,26] which, in principle, is iterative in type:[27] an arbitrarily but conveniently chosen pseudo-stationary radical profile serves as a starting point for an improved profile, which is calculated by developing the growth process (correctly considering the chain-length dependence of k_t) in the presence of the radical population given by the initial profile, moving from one of the L_0 intervals (of duration ($k_p[\mathrm{M}]^{-1}$), which is the average time necessary to complete one propagation step) to the next. The Poissonian character of the growth process is taken into account by making allowance for an in situ Poisson broadening, thus breaking the strict coupling between time and the degree of polymerization. In the next iteration step, the improved profile forms the new radical concentration for the growth process and the procedure is continued until further cycles of iteration do not produce any further change. From these parameters, the CLD of the dead polymer can be calculated for disproportionation and combination, including its moments, by simply recording the changes that occur when passing from one time interval to the next. The chain-length dependence of k_t was introduced in form of the geometric mean approximation[28]

$$k_t^{(x,y)} = k_t^{(1,1)}(xy)^{-b/2} \tag{9}$$

which characterizes each individual termination process between two radical chains of lengths x and y, where the quantity $k_t^{(1,1)}$ is the (hypothetical) constant that describes the termination behavior of two chains, each with a length of unity.

For the simulation of a GPC broadening (i.e., the axial dispersion), the following equation was applied on the original hyper mass distribution (w) to obtain the SEC distribution (w^{SEC}):

$$w^{\mathrm{SEC}}(\log j) = \int_0^\infty \frac{w(\log j)}{\sqrt{2\pi}\,\sigma_{\mathrm{ad},k}} \exp\left[-\frac{(\log j - \log l)^2}{2\sigma_{\mathrm{ad},k}^2}\right]\frac{1}{f(\log l)}\,\mathrm{d}(\log l) \quad (10)$$

where f is a normalizing factor that is dependent on l:

$$f(\log l) = \int_0^\infty \frac{1}{\sqrt{2\pi}\,\sigma_{\mathrm{ad},k}} \exp\left[-\frac{(\log i - \log l)^2}{2\sigma_{\mathrm{ad},k}^2}\right]\mathrm{d}(\log i) \quad (11)$$

The factor f is introduced to compensate the loss of polymer chains that are (formally) shifted to negative chain lengths, because of the Gaussian form of the dispersion function (thus, the originally normalized distribution is kept normalized). Originally, eq 10 (without the normalizing factor f) was reported by Tung[29] (and later also applied by Buback et al.[16]) to simulate the SEC broadening on PLP-derived CLDs. The distribution curves were calculated for $\sigma_{\mathrm{ad},k} = 0.00$, 0.025, 0.05, and 0.075; some of the data for $\sigma_{\mathrm{ad},k} = 0.05$ (function X, see below) was taken from ref 21.

The results described in this communication are based on the first extra peak of hyper mass distributions using a linear (not a logarithmic) abscissa: The positions of the low-molecular-weight (and high-molecular-weight) side points of inflection l_{LPI} (and l_{HPI}) are determined from the maximum and minimum of the first derivative (derived with the three-point formula) of the distribution curve and l_{MAX} characterizes the position of the peak maximum of the distribution curve between the two points of inflection.

Results and Discussion

Certainly, the overall width (δ_{E}) of a peak of a CLD, be it experimental or simulated, is composed of all the factors that may produce "broadness" in the range of chain lengths that surround a PLP peak, such as (i) the "kinetic" polydispersity due to the different amplitudes of the individual degrees of polymerization, as manifested in curve a of Figure 1a or 1b, (ii) the (Poissonian) polydispersity produced by the genuine fluctuation of propagation, and finally (iii) the "apparent" polydispersity caused by the SEC detection device when the CLD is analyzed. Of these three factors, the latter two are considered in the quantity δ_{T}. Therefore, it is our conviction that the deviations of l_{LPI} and l_{MAX} from L_0, expressed by the correction factors L_0/l_{LPI} and L_0/l_{MAX}, respectively, must be describable as unique functions of some combination (difference or ratio) of δ_{E} and δ_{T} if they are associated with the broadness or asymmetry of the peak shown in curve a of Figure 1a and 1b. Many of such combinations might work; however, we have restricted ourselves to the following:

$$X \equiv (\log \delta_{\mathrm{E}})^2 - (\log \delta_{\mathrm{T}})^2 \quad (12)$$

$$Y \equiv \frac{\delta_{\mathrm{E}} - 1}{\delta_{\mathrm{T}} - 1} - 1 \quad (13)$$

$$Z \equiv \frac{\ln \delta_{\mathrm{E}}}{\ln \delta_{\mathrm{T}}} - 1 \quad (14)$$

(The subtraction of unity in the expressions for Y and Z makes them start with meaningful values at $Y = 0$ and $Z = 0$, respectively.) Function X derives its legitimacy from the fact that it should represent some measure of the kinetically controlled peak width of the peak unbroadened by Poissonian and other (Gaussian) fluctuation processes (see curve a of Figure 1a or 1b). Function Y is rather empiric in character but proved to give reasonable results, whereas function Z is related to function Y by a (backward) series expansion of ln δ_{E} and ln δ_{T}, respectively ($\ln \delta = \ln[1 + (\delta - 1)] \approx \delta - 1$).

The correction factors L_0/l_{LPI} and L_0/l_{MAX} can be well-represented as linear functions of Θ (where Θ is X, Y, or Z) in the forms

$$\frac{L_0}{l_{\mathrm{LPI}}} = I - S\cdot\Theta \quad (15)$$

$$\frac{L_0}{l_{\mathrm{MAX}}} = I - S\cdot\Theta \quad (16)$$

respectively, for each of the $\sigma_{\mathrm{ad},k}$ values investigated ($\sigma_{\mathrm{ad},k} = 0.00$, 0.025, 0.05, 0.075). The parameters of these linearizations (intercepts I and slopes S) were evaluated for all CLDs (termination by disproportionation and combination together, D + C), as well as for each of the two modes separately (in the latter case, more-accurate corrections will be accessible if the mode of termination is known). They are listed in Table 1 in the form of the intercepts (I) and slopes (S) of the linearizations. In all instances, the intercepts concerning L_0/l_{MAX} are fairly close to unity (with a tendency to increase as $\sigma_{\mathrm{ad},k}$ increases), which means that $X = 0$ ($Y = 0$, $Z = 0$) corresponds to conditions where l_{MAX} is a fair representative of L_0 (the high termination rate limit). The intercepts for L_0/l_{LPI} are markedly larger and exhibit the same tendency of increasing as $\sigma_{\mathrm{ad},k}$ increases, emphasizing the fact that, in the high termination rate limit, l_{LPI} is not the optimum substitute for L_0, especially if the axial dispersion is high. The slopes are negative throughout, for L_0/l_{LPI} and L_0/l_{MAX}. Thus, (comparatively) high values of X (Y, Z), which are typical of the low termination rate limit, where l_{LPI} is the better estimate, make L_0/l_{LPI} approach unity and let L_0/l_{MAX} sensibly digress from unity. The mean error that remains after application of the correction factor L_0/l_{LPI} is about 0.5% if disproportionation or combination data are considered separately and slightly larger if no discrimination is made between the two modes of termination, regardless of which correction function (X, Y, or Z) is applied. The maximum error does not exceed 2%. The situation is slightly less satisfactory for the correction factor L_0/l_{MAX}: here, the remaining error is ~2%, on average, with scarcely a deterioration to be seen if no information is available on the mode of determination, again independent of which function is applied. With respect to the maximum remaining deviation, however, markedly higher values are observed (up to 10%), especially for the larger values of $\sigma_{\mathrm{ad},k}$ ($\sigma_{\mathrm{ad},k} = 0.05$ and 0.075). In all, X is the function that works best in this context.

Closer inspection of these data for I and S reveals that, in most cases, there is a strong increase in (the absolute values of) I and S, relative to increasing σ (the subscript "ad,k" is now dropped, for convenience). The further procedure intends to correlate the parameters (slopes and intercepts) listed in Table 1 with σ, to be

Table 1. Intercepts (*I*) and Slopes (*S*) of the Correction Factors Obtained for Individual $\sigma_{ad,k}$ Values Regarding Either Disproportionation (D) or Combination (C), as Well as Using All Data (D + C)

	disproportionation (D)		combination (C)		all data (D + C)	
$\sigma_{ad,k}$	*I*	*S*	*I*	*S*	*I*	*S*
			$L_0/l_{LPI} = I - SX$			
0.000	1.020	0.495	1.014	2.80	1.017	1.49
0.025	1.048	3.21	1.041	4.72	1.045	3.66
0.050[a]	1.118	6.80	1.104	7.41	1.112	7.14
0.075	1.224	16.1	1.185	10.14	1.210	13.4
			$L_0/l_{LPI} = I - SY$			
0.000	1.037	0.067	1.023	0.049	1.033	0.064
0.025	1.061	0.090	1.050	0.092	1.057	0.092
0.050	1.117	0.172	1.101	0.176	1.112	0.178
0.075	1.223	0.718	1.208	0.606	1.218	0.673
			$L_0/l_{LPI} = I - SZ$			
0.000	1.038	0.074	1.023	0.052	1.033	0.070
0.025	1.061	0.102	1.050	0.101	1.057	0.103
0.050	1.117	0.205	1.101	0.207	1.112	0.212
0.075	1.223	0.874	1.211	0.766	1.219	0.833
			$L_0/l_{MAX} = I - SX$			
0.000	0.966	18.7	0.963	24.0	0.965	20.9
0.025	0.972	17.8	0.969	21.0	0.970	18.8
0.050	0.998	19.7	0.982	19.9	0.992	19.9
0.075	1.055	33.5	1.006	22.5	1.026	26.5
			$L_0/l_{MAX} = I - SY$			
0.000	0.967	0.157	0.966	0.178	0.967	0.171
0.025	0.971	0.233	0.967	0.256	0.969	0.240
0.050[b]	0.980	0.428	0.960	0.416	0.973	0.429
0.075	1.034	1.308	1.042	1.246	1.028	1.202
			$L_0/l_{MAX} = I - SZ$			
0.000	0.961	0.148	0.957	0.166	0.961	0.162
0.025	0.969	0.252	0.962	0.266	0.966	0.257
0.050	0.979	0.503	0.959	0.482	0.973	0.502
0.075	1.032	1.572	1.046	1.559	1.028	1.472

[a] Values are based on an extended dataset and, therefore, are slightly different from those in eqs 8, 8a, and 8b of ref 21. [b] Values are based on an extended dataset and, therefore, are slightly different from those in eqs 9, 9a, and 9b of ref 21.

Table 2. Parameters of Unified Correction Functions for Termination by Disproportionation (D), Combination (C), or Unknown Termination (D + C)

	I_I	S_I	α	I_S	S_S	β
			$L_0/l_{LPI} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})X$			
D	1.024	35.88	2	0.775	2690	2
C	1.020	30.09	2	3.566	1240	2
D + C	1.022	33.89	2	1.922	2060	2
			$L_0/l_{LPI} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})Y$			
D	1.038	32.66	2	0.066	20480	4
C	1.025	32.22	2	0.068	17020	4
D + C	1.033	32.56	2	0.070	19000	4
			$L_0/l_{LPI} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})Z$			
D	1.038	32.58	2	0.073	25170	4
C	1.024	32.84	2	0.071	21950	4
D + C	1.034	32.73	2	0.076	23830	4
			$L_0/l_{MAX} = I_I - I_SX$			
D	0.979			18.43		
C	0.964			18.34		
D + C	0.973			18.54		
			$L_0/l_{MAX} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})Y$			
D	0.966	157	3	0.152	2700	3
C	0.957	186	3	0.172	2500	3
D + C	0.964	145	3	0.171	2420	3
			$L_0/l_{MAX} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})Z$			
D	0.963	162	3	0.151	3330	3
C	0.951	212	3	0.160	3260	3
D + C	0.960	157	3	0.168	3060	3

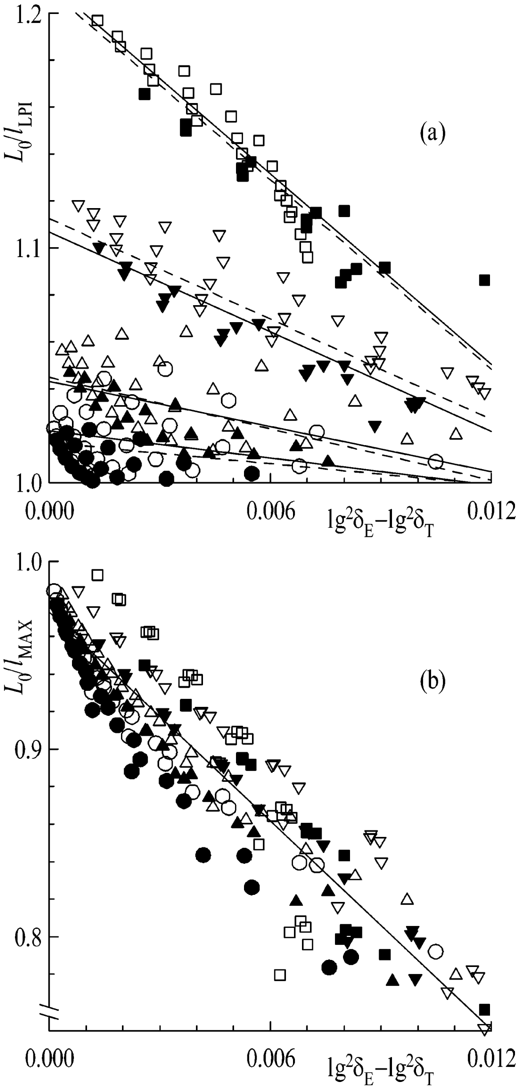

Figure 2. Correction factors (a) L_0/l_{LPI} and (b) L_0/l_{MAX} versus $X \equiv (\log \delta_E)^2 - (\log \delta_T)^2$ for $\sigma_{ad,k} = 0.00$ (circles), $\sigma_{ad,k} = 0.025$ (triangles), $\sigma_{ad,k} = 0.050$ (inverted triangles), and $\sigma_{ad,k} = 0.075$ (squares), calculated for termination by disproportionation (open symbols) and combination (full symbols). Broken lines refer to corrections for individual $\sigma_{ad,k}$ values (see column D + C in Table 1 corresponding to *X* for parameters). Full lines represent unified correction functions (see row D + C in Table 2 referring to *X*). Some of the data for $\sigma_{ad,k} = 0.050$ has been reproduced from ref 21.

able to predict correction factors for *any* extent of axial dispersion. The general formulas to which the data were fitted are

$$\frac{L_0}{l_{LPI}} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})\Theta \tag{17}$$

and

$$\frac{L_0}{l_{MAX}} = (I_I + S_I\sigma^{\alpha}) - (I_S + S_S\sigma^{\beta})\Theta \tag{18}$$

where Θ is *X*, *Y*, or *Z*, I_I and S_I are the respective intercepts and slopes of the plots of intercepts *I* originating from the *individual* linearizations versus σ^{α}, and I_S and S_S are the corresponding quantities that result from linearizations of *S* vs σ^{β}. Because of the rather strong dependence of *I* and *S* on σ, this procedure works well except for one specific system (see below), although it is not always the same power of σ that gives the best

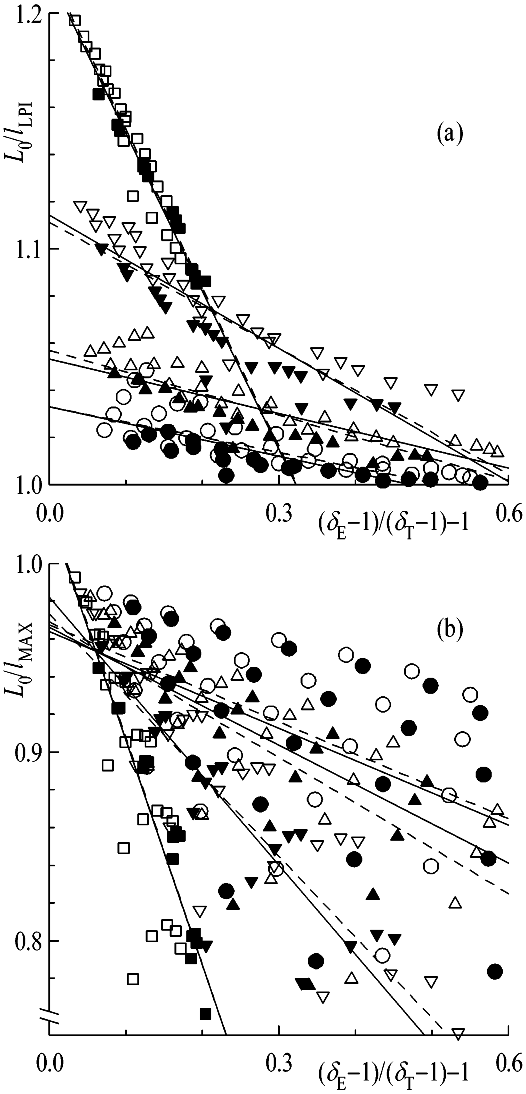

Figure 3. Correction factors (a) L_0/l_{LPI} and (b) L_0/l_{MAX} versus $Y \equiv (\delta_E - 1)/(\delta_T - 1) - 1$ for $\sigma_{ad,k} = 0.00$ (circles), $\sigma_{ad,k} = 0.025$ (triangles), $\sigma_{ad,k} = 0.050$ (inverted triangles), and $\sigma_{ad,k} = 0.075$ (squares), calculated for termination by disproportionation (open symbols) and combination (full symbols). Broken lines refer to corrections for individual $\sigma_{ad,k}$ values (see column D + C in Table 1 corresponding to Y for parameters). Full lines represent unified correction functions (see row D + C in Table 2 referring to Y).

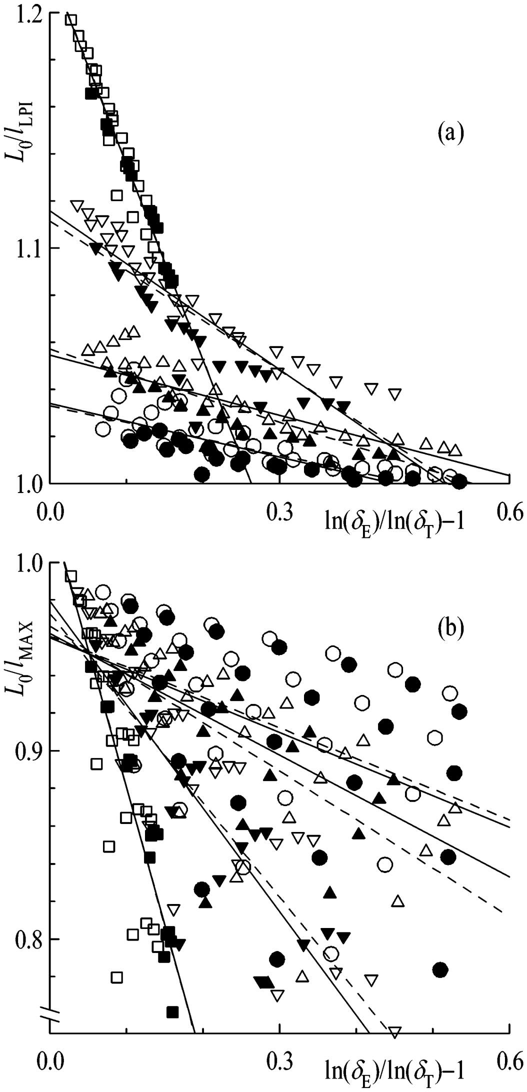

Figure 4. Correction factors (a) L_0/l_{LPI} and (b) L_0/l_{MAX} versus $Z \equiv (\ln \delta_E)/(\ln \delta_T) - 1$ for $\sigma_{ad,k} = 0.00$ (circle), $\sigma_{ad,k} = 0.025$ (triangles), $\sigma_{ad,k} = 0.050$ (inverted triangles), and $\sigma_{ad,k} = 0.075$ (squares), calculated for termination by disproportionation (open symbols) and combination (full symbols). Broken lines refer to corrections for individual $\sigma_{ad,k}$ values (see column D + C in Table 1 corresponding to Z for parameters). Full lines represent unified correction functions (see row D + C in Table 2 referring to Z).

fit. The parameters of this “unified” fit are given in Table 2, together with the associated powers of σ that are responsible for the best fit (also see Figures 2a, 3 (a and b), and 4 (a and b). Note that the remaining average error after correction with L_0/l_{LPI} or L_0/l_{MAX} is only slightly increased (by a factor of 1.5 at most) when the masterfunction is applied (compared to the application of eqs 15 and 16, using the parameters constructed separately for individual σ values, given in Table 1), whereas the maximum error does not seem to be affected at all. However, as already mentioned previously, there is one case where the otherwise general trends regarding the dependence on σ are not fulfilled (L_0/l_{MAX} for function X), so that the usual treatment that could be applied to all other systems is not meaningful here. In this case, it seems to be recommendable to make a virtue of necessity and construct a masterfunction by considering *all* individual $L_0/l_{MAX}-X$ pairs *together*, irrespective of the σ value, and constructing a linear relationship of the type of eq 16, as was done in the evaluation of the data given in Table 1 for each specific value of σ; however, now, the evaluation is done for all the data involved (see Figure 2b). It is clear that the correction factors obtained in this way certainly will work somewhat less satisfactorily than those which originate from the other correlations; however, (i) contrary to these observations, the specific σ value does not enter explicitly into the procedure (only via eq 6, when calculating the variable X), which makes the calculation less sensible toward the choice of σ, and (ii) the loss in accuracy seems to be rather limited (the remaining mean error never exceeds 3%). Thus, they might serve as a fair access to improved L_0 data if nothing is known about the extent of axial dispersion. It should be emphasized that this seems to be a unique property of the correction factor L_0/l_{MAX} when plotted against X: an inspection of all the other plots shown in Figures 2−4 (except Figure 2b, of course) reveals that

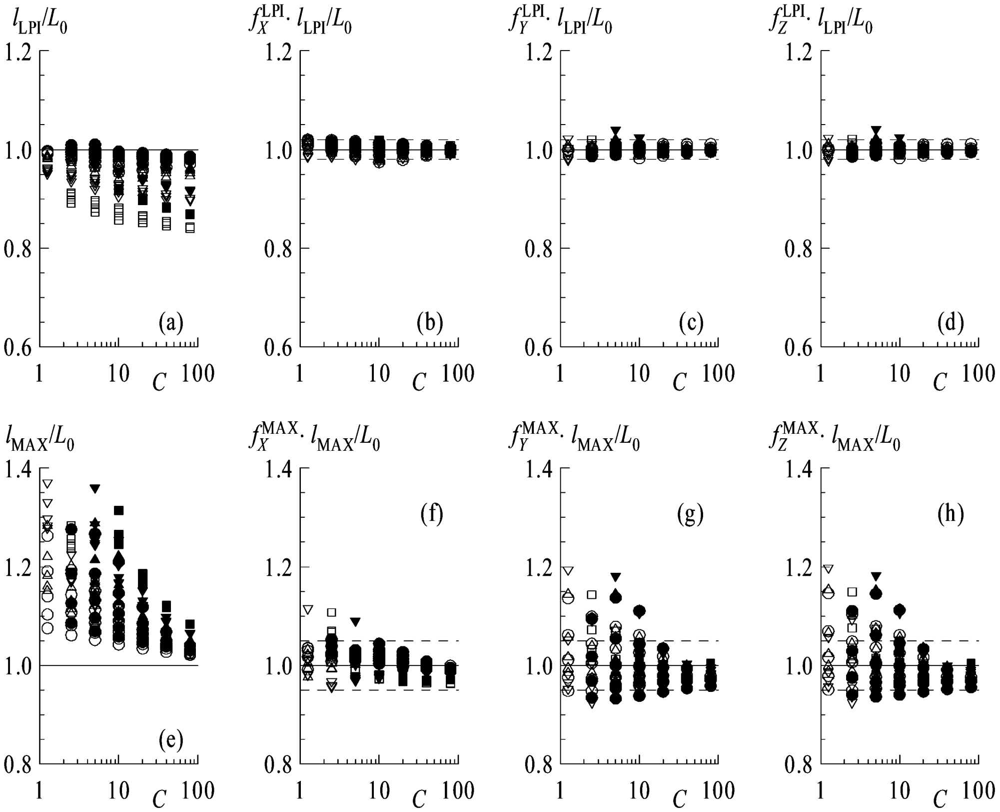

Figure 5. Plots of (a−d) l_{LPI}/L_0 and (e−h) l_{MAX}/L_0 versus log C. Panels a and e show uncorrected values, whereas other panels show corrected values using correction functions obtained for X (panels b and f), Y (panels c and g), and Z (panels d and h). Legend is as follows: circles, $\sigma_{ad,k} = 0.00$; triangles, $\sigma_{ad,k} = 0.025$; inverted triangles, $\sigma_{ad,k} = 0.050$; and squares, $\sigma_{ad,k} = 0.075$, calculated for termination by disproportionation (open symbols) and combination (full symbols). Broken lines give 2% limits (panels b−d) or 5% limits (panels f−h). Some of the data for $\sigma_{ad,k} = 0.050$ has been taken from ref 21.

such a procedure of plotting *all* the data points, irrespective of the σ value underlying their generation, would lead to unsatisfactory or even worthless results.

Conclusions and Outlook

In summary, the previously outlined procedure leads to a substantial improvement of the theoretical basis of the evaluation of the quantity L_0 that is necessary for the determination of k_p by means of the pulsed laser polymerization−size exclusion chromatography (PLP−SEC) method, with a slight preference to perform the correction via L_0/l_{LPI}. The only prerequisite is a fair knowledge of the quantity σ. This is accessible rather easily by means of a recently described procedure.[30] For the data used in the aforementioned treatment, the use of *uncorrected* l_{LPI} values as a substitute of L_0 would produce an average error of ≈2%−12% (the lower boundary refers to $\sigma = 0$, and the upper bound refers to $\sigma = 0.075$) and maximum errors of ≈3%−16%. The situation would be even worse if l_{MAX} were used without correction: the corresponding figures are ≈8%−15% for the mean error and ≈10%−40% for the maximum error, again depending on σ. Thus, the application of any of the corrections developed is believed to provide a sensible improvement of the situation. The full account of the extent of improvement is given by Figure 5, which demonstrates how the error caused by the direct use of raw data is reduced by the correction functions based on X, Y, and Z. The remaining average error is <1% if the analysis is based on l_{LPI} and ca. 3% for l_{MAX} for any value of the σ operative. However, recall that all these corrections exclusively refer to the *theoretical* basis of the evaluation of k_p and cannot reduce other *experimental* errors involved in the evaluation of chain-length distributions (CLDs) and their characteristic points (points of inflection, maxima) by the SEC techniques (e.g., those resulting from calibration problems). Accordingly, increased efforts should be directed toward removing these shortcomings, to be able to take full advantage of the achievements obtained in this investigation. Nevertheless, a revision of older k_p data, according to the lines presented in this communication, could at least eliminate some of the remaining inaccuracy that is involved. In principle, the reconstruction of the σ values pertinent to these investigations would be easily possible if only CLDs of narrow-distributed standards are still available.[19] If not, with the help of a reasonable estimate of σ (usually σ does not vary appreciably, even over long periods, if no change of the experimental setup has been made), especially, function X still might do a good job in transforming the positions of the maxima l_{MAX} into the characteristic chain length L_0 necessary for evaluating k_p. As a closing point, even the evaluation of CLDs by the matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) method, where l_{LPI} and l_{MAX} certainly do not suffer from distortion by axial dispersion, might profit from the correction functions developed in this communication: formally, the case corresponds to $\sigma = 0$, so that the l_{LPI} and l_{MAX} data derived from MALDI−TOF CLDs can be improved through application of the proper correction factor.

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