Macromolecules **1996,** *29,* 7727−7733 **7727**

Use of Chain Length Distributions in Determining Chain Transfer Constants and Termination Mechanisms

Graeme Moad* and Catherine L Moad

CSIRO Division of Chemicals and Polymers, Private Bag 10, Clayton South MDC, Victoria 3169, Australia

Received June 11, 1996; Revised Manuscript Received September 10, 1996[⊗]

ABSTRACT: A new method for determining transfer constants based on an analysis of the ln chain length (or molecular weight) distributions has recently been reported. In this paper, the basis of this method is examined in terms of classical statistics and with the aid of simulated chain length distributions. The advantages, limitations and sources of error in the method are considered with reference to conventional analysis. We show that one major benefit is that the requisite information can be obtained by analysis of a small segment of the chain length distribution. This means that it may be applied under circumstances where there may be overlap between the distributions of the new polymer being formed and the transfer agent (*i.e.* transfer constants to polymeric species can be determined). The method also has general application since it is less sensitive to experimental noise, poor baseline selection, or the presence of artifacts in gel permeation chromatograms. Finally we look at the scope for obtaining additional mechanistic information on termination mechanisms by analysis of chain length distributions of low-conversion polymers by considering the effects of combination:disproportionation ratios and chain length dependent propagation and termination.

Introduction

In free-radical polymerization, added transfer agents may be used to control (a) the polymer molecular weight, (b) the polymerization rate (by mitigating the gel or Trommsdorff effect), and (c) the nature of the polymer end groups. Transfer agents thus find widespread use in both industrial and laboratory polymer syntheses. General aspects of chain transfer have been reviewed by Barson,[1] Farina,[2] and Palit *et al.*[3] and their use in producing oligomers and functional polymers has been reviewed by Corner[4] and Starks.[5]

A knowledge of kinetics and mechanisms of chain transfer is thus of great importance to the understanding and commercial application of free radical polymerization and has been a subject of ongoing research in these laboratories.

Statistics of Free Radical Polymerization with Chain Transfer

According to the classical mechanism for free radical polymerization (Scheme 1), a propagating radical $P_i^\bullet$, once generated, has only three options. It can propagate (add monomer), it can undergo termination by radical−radical reaction, or it can react by chain transfer. Chain transfer involves the reaction of a propagating chain ($P_i^\bullet$) with a transfer agent to terminate one polymer chain and produce a new radical ($T^\bullet$) which initiates a new chain ($P_1^\bullet$).[6] The substrate for chain transfer may be a chain transfer agent (T) or it may be the initiator (I), the monomer (M), or some other component of the polymerization medium.[7]

Scheme 1

Initiation:

$$I_2 \xrightarrow{k_d} 2I\bullet$$

$$I\bullet + M \xrightarrow{k_i} P_1\bullet$$

Propagation:

$$P_i\bullet + M \xrightarrow{k_p} P_{i+1}\bullet$$

Termination:

$$P_i\bullet + P_j\bullet \xrightarrow{k_{tc}} P_{i+j}$$

$$P_i\bullet + P_j\bullet \xrightarrow{k_{td}} P_i + P_j$$

Chain Transfer:

$$P_i\bullet + T \xrightarrow{k_{tr\ T}} P_i + T\bullet$$

$$T\bullet + M \xrightarrow{k_{s\ M}} P_1\bullet$$

$$P_i\bullet + I_2 \xrightarrow{k_{tr\ I}} P_i + I\bullet$$

$$P_i\bullet + M \xrightarrow{k_{tr\ M}} P_i + P_1\bullet$$

At any given instant of the polymerization process, the probability of propagation, S, is simply the rate of propagation divided by the sum of all possible fates of the propagating radical (eq 1).[8,9]

$$S = \frac{R_p}{R_p + R_{tr} + R_t} \tag{1}$$

where

$$R_p = k_p[M][P^\bullet] \tag{2}$$

$$R_{tr} = k_{trT}[T][P^\bullet] + k_{tr\ I}[I][P^\bullet] + k_{tr\ M}[M][P^\bullet] \tag{3}$$

$$R_t = k_t\,[P^\bullet]^2 \tag{4}$$

and

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* Author to whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

$$k_t = k_{tc} + k_{td}$$

thus

$$S = (k_p[M][P^\bullet])/(k_p[M][P^\bullet] + k_{trT}[T][P^\bullet] + k_{trI}[I][P^\bullet] + k_{trM}[M][P^\bullet] + k_t[P^\bullet]^2) \quad (5)$$

$$= 1/(1 + C_T[T]/[M] + C_I[I]/[M] + C_M + k_t[P^\bullet]/k_p[M]) \quad (6)$$

or

$$\frac{1}{S} = 1 + C_T\frac{[T]}{[M]} + C_I\frac{[I]}{[M]} + C_M + \frac{k_t[P^\bullet]}{k_p[M]} \quad (7)$$

where C_T, C_M, and C_I are the transfer constants for transfer to transfer agent, monomer, and initiator, respectively ($=k_{trT}/k_p$, *etc.*).

The probability that a chain will propagate and terminate to give length i is the product of the probability of the individual propagation steps and the probability of termination at that chain length. If termination is independent of chain length, this can be expressed as the probability of propagation raised to the power $(i - 1)$ multiplied by the probability of termination $(=1 - S)$. Thus the (instantaneous) chain length distribution is

$$P_i = (1 - S)S^{i-1} \quad (8)$$

This is the well-known Schulz–Flory most probable distribution,[6,8–11] for which

$$\bar{X}_n = \frac{1}{1 - S} \quad (9)$$

and

$$S = 1 - \frac{1}{\bar{X}_n} \quad (10)$$

Substitution for S in eq 7 gives the Mayo equation (eq 11).

$$\frac{1}{\bar{X}_n} = C_T\frac{[T]}{[M]} + C_I\frac{[I]}{[M]} + C_M + \frac{k_t[P^\bullet]}{k_p[M]} \quad (11)$$

or since in the absence of added transfer agent

$$\frac{1}{\bar{X}_{n\phi}} = C_I\frac{[I]}{[M]} + C_M + \frac{k_t[P^\bullet]}{k_p[M]} \quad (12)$$

it follows that

$$\frac{1}{\bar{X}_n} = C_T\frac{[T]}{[M]} + \frac{1}{\bar{X}_{n\phi}} \quad (13)$$

Transfer Constant Measurement from Gel Permeation Chromatography (GPC) Data

The most used method of evaluating transfer constants is by application of the simplified form of the Mayo equation (eq 13). It follows from eq 13 that a plot of $1/\bar{X}_n$ *vs* [T]/[M] should yield a straight line with slope C_T and intercept $1/\bar{X}_{n\phi}$.[12] The usual experimental procedure involves evaluations of $\bar{X}_n$ for very low-conversion polymerizations (such that the value of [T]/[M] remains essentially constant). Determinations for more than three concentrations of added transfer agent are usually preferred.

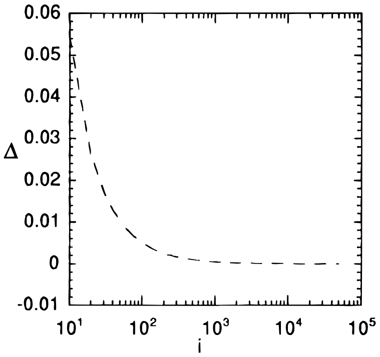

Figure 1. Fraction (△) by which $1 - 1/S$ exceeds ln S as a function of the degree of polymerization (i).

The values of $\bar{X}_n$ are most commonly obtained by GPC analysis. Problems arise because this analysis is sensitive to baseline fluctuations (see below) and the presence of impurities. Furthermore, it cannot be easily applied in the case of macromolecular transfer agents when the molecular weight distributions of the chain transfer agent and formed polymer may overlap.

Recently Gilbert and co-workers[13–15] have pointed out that information on transfer constants can also be obtained by appropriate analysis of the molecular weight distribution obtained by GPC. Equation 14[14] was derived from an analysis of the kinetics of emulsion polymerization but is generally applicable.

$$\lim_{i\to\infty,[I]\to 0} P_i \propto \exp\left\{-\frac{k_{trM}[M] + k_{trT}[T]}{k_p[M]}i\right\} \quad (14)$$

Differentiation of this relationship indicates that the limiting slope of a plot of ln P_i *vs* i will be

$$\frac{d(\ln P_i)}{di} = -\left\{\frac{k_{trM}[M] + k_{trT}[T]}{k_p[M]}\right\} = -\left\{C_M + C_T\frac{[T]}{[M]}\right\} \quad (15)$$

This method of analysis has also been adopted by Hutchinson *et al.*[16] to evaluate transfer constants from molecular weight distributions obtained by pulsed laser photolysis.

It follows from eqs 7 and 9 that this slope can also be expressed as.

$$\frac{d(\ln P_i)}{di} = 1 - \frac{1}{S} = -\frac{1}{(\bar{X}_n - 1)} \quad (16)$$

Further understanding of the method can be gained by considering the basis of the method in terms of classical chain statistics. Recalling from eq 8 that $P_i = (1 - S)S^{i-1}$, then

$$\frac{d(\ln P_i)}{di} = \ln S \quad (17)$$

This indicates that a plot of the ln chain length distribution (ln P_i) *vs* i (ln CLD plot) should give a straight line with slope ln S. Since values of $1 - 1/S$ and ln S converge (difference *ca.* 5% for $\bar{X}_n = 10$ and <1% for $\bar{X}_n > 50$; see Figure 1), this equation (eq 17) is

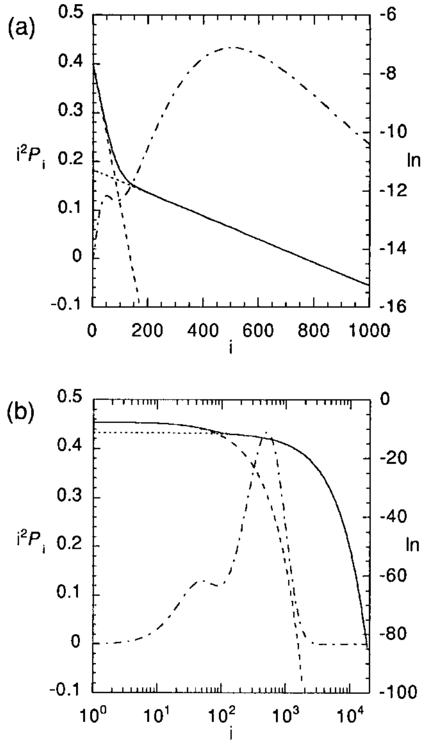

Figure 2. Simulated ln CLD plots for polymer $\bar{X}_n = 250$ (···) ($S_o = 0.999$, $\bar{X}_n = 1000$, $C_T = 0.3$, [T]/[M] = 0.01), polymer $\bar{X}_n = 20$ (- - -), a 80:20 blend of the two polymers (—), and a simulated "GPC trace" for the blend (— • —). Graph of (a) linear *x*-axis (b) log *x*-axis.

equivalent to that of Gilbert and co-workers[13,14] (eq 15) for polymers of sufficiently high molecular weight.

The evaluation of transfer constants can then be carried out in a manner similar to the conventional Mayo analysis. If termination by combination and transfer to initiator and monomer are negligible, eq 7 becomes

$$\frac{1}{S} = 1 + \frac{1}{\bar{X}_{n\phi}} + C_T\frac{[T]}{[M]} \tag{18}$$

The transfer constant can then be obtained from the slope of a plot of $1/S - 1$ *vs* [T]/[M] and the intercept will be $1/X_{n\phi}$. However, since $1/S - 1 = -(1 - 1/S) \sim \ln S$ (see above), the slopes of the ln CLD plots can be plotted *vs* [T]/[M] with similar results.

Gilbert *et al.* recommend taking only the high molecular weight end of the distribution since this is less likely to be affected by the occurrence of other termination mechanisms (*i.e.* combination; see below) or the effects of chain length dependent termination. However, if these effects are negligible (and they often are; see the discussion below), then values of S and hence $\bar{X}_n$ and C_T can, in principle, be evaluated from any part of the ln CLD plot. *It is not necessary to analyze the entire chain length distribution.* This finding is particularly useful when measuring transfer constants to polymeric species where the chain length distributions of the "transfer agent" and the polymer being formed may overlap, making it difficult or impossible to evaluate $\bar{X}_n$ by applying standard GPC software.

This application is illustrated in Figure 2 for a blend of a polymer $\bar{X}_n = 250$ and another polymer with $\bar{X}_n = 20$ (both polymers have $\bar{X}_w/\bar{X}_n = 2.0$). The chain length distributions overlap, making estimation of $\bar{X}_n$ of the higher molecular weight component by conventional analysis difficult. However, for $i > 200$, the slope of the ln CLD plot is not affected (<0.1%) by the contribution of the lower molecular weight polymer (see Figure 2a). The slope of the ln CLD plot of the blend for small i is dominated by the contribution from low molecular weight polymer (see Figure 2b). Thus, for low-conversion polymers, a knowledge of the limiting slopes of the ln CLD plot (as $i \to 0$ and as $i \to \infty$) may offer a method of resolving a bimodal molecular weight distribution into its component parts.

The method also has general application and is particularly useful if signal to noise is poor for two reasons. (a) Only that part of the molecular weight distribution with adequate signal to noise need be used. The high and low molecular weight tails, which are most sensitive to noise and can have a large influence on $\bar{X}_n$, need not be considered. Evaluation of $\bar{X}_n$ using conventional GPC software requires analysis of the entire distribution. (b) In a similar way, the effects of problems due to instrumental and other baseline artifacts can be eliminated.

As a consequence of these factors, values of C_T obtained by this method are generally less sensitive to experimental noise than those obtained using the Mayo method.

It also follows that analysis of the linearity of the ln CLD plot can be used to establish the quality of a GPC chromatogram and the adequacy of baseline selection or, if these are established, the method can be used to test the validity of mechanistic assumptions.

Effects of Termination Mechanism on the ln Chain Length Distribution and the Values of Measured Transfer Constants

It has been assumed in the above derivation of the ln CLD method that termination is solely by disproportionation or chain transfer.

Gilbert and co-workers[13,14] have indicated that by examining only the high molecular weight tail of the distribution (the limit as $i \to \infty$), the effects of some termination by combination and the chain length dependence of propagation and termination rate constants on the slope of a ln CLD plot should be negligible. However, the exact magnitude of the errors and the specific conditions for obtaining the slope were not clearly delineated.

If the classical mechanism (Scheme 1) applies, then, for a given value of S (or $\bar{X}_n$), there are simple relationships between the chain length distribution and the probability of propagation.[6,9,11] If termination is solely by disproportionation or chain transfer, then eq 17 applies and the slope of the ln CLD plot is ln S.

On the other hand, if termination is wholly by combination, then the instantaneous chain length distribution is[11,17]

$$P_i = (i - 1)(1 - S)^2 S^{i-2} \tag{19}$$

The slope of the ln CLD plot will then be

$$\frac{\mathrm{d}(\ln P_i)}{\mathrm{d}i} = \ln S + \frac{1}{i - 1} \tag{20}$$

For large i the second term of eq 20 becomes negligible and the limiting slope will be the same as for termination by disproportionation (eq 21).

$$\lim_{i\to\infty}\frac{\mathrm{d}\{\ln[(i-1)(1-S)^2S^{i-2}]\}}{\mathrm{d}i} = \ln S \qquad (21)$$

However, for the $1/(i-1)$ term to be negligible ($<1\%$) with respect to $\ln S$, then i must be $>50\bar{X}_n$ [for termination by combination,[6] $\bar{X}_n = 2/(1-S)$]. Under these conditions, signal-to-noise is likely to be a serious problem in GPC analysis (cf. Figure 3a,b). However, since i is a known quantity, it would be possible to subtract $1/(i-1)$ from the derivative of the ln CLD plot to yield a straight line. For a polymerization where termination is solely by combination, the value of $\mathrm{d}(\ln P_i)/\mathrm{d}i - 1/(i-1) = \ln S$.

If termination is by a mixture of combination and disproportionation, then a weighted sum of eqs 8 and 19 will give the chain length distribution. Values of k_{td}/k_{tc} for many polymerizations have been determined.[18,19] The expression for the overall chain length distribution must also take into account that whereas disproportionation gives two chains, combination gives only one chain.

If termination is by a mixture of combination, disproportionation, and chain transfer, expressions for the fraction of chains terminating by the various mechanisms are required. If the number of chains formed by combination and disproportionation is not affected by the occurrence of chain transfer (this is true if there is no retardation), the fraction of termination by radical–radical reaction is given by the expression

$$r = \frac{1 - S_\phi}{1 - S_\phi + C_T\dfrac{[T]}{[M]}} \qquad (22)$$

where S_ϕ is the probability of propagation in the absence of chain transfer. Note that $1/(1 - S_\phi)$ is equal to $\bar{X}_{n\phi}$ if all termination is by disproportionation.

If the fraction of chains terminating by combination is r_c, then

$$P_i = rr_c(i-1)(1-S)^2S^{i-2} + r(1-r_c)(1-S)S^{i-1} + (1-r)(1-S)S^{i-1} \qquad (23)$$

and in the high molecular weight limit $\mathrm{d}(\ln P_i)/\mathrm{d}i$ will converge to $\ln S$.

$$\lim_{i\to\infty}\frac{\mathrm{d}(\ln P_i)}{\mathrm{d}i} = \ln S \qquad (24)$$

It is noteworthy that, irrespective of termination mechanism, the limiting slope will give a value of S which can be directly related to the average chain length of the propagating species involved in termination (eq 9). It follows that if the effects of chain length dependent termination could be ignored (see below), given an independent determination of $\bar{X}_n$ or S (*e.g.* by integration of the GPC trace), a very simple method of determining the combination:disproportionation ratio exists. Under these circumstances, the direct fitting of eq 23 to chain length distributions by applying nonlinear regression techniques might also be used to give values of r, r_c, and S.

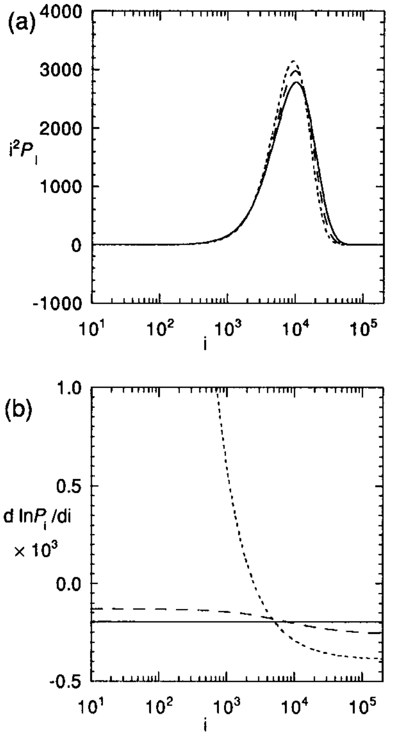

Figure 3. (a) "GPC trace" and (b) derivative of the ln CLD plot for polymers of the same number average degree of polymerization ($\bar{X}_n = 5153$) but with termination by 100% combination (···), 70% combination (- - -), or 0% combination (—). The distributions were calculated using eq 23.

Effects of Chain Length Dependent Termination Mechanism on the ln Chain Length Distribution

It is now generally accepted that termination in radical polymerization is chain length dependent and a number of papers have appeared on the influence of chain length dependent termination on molecular weight distributions.[14,20–22]

Bamford[20] and Olaj *et al.*[22] have considered the effect of chain length dependent termination on the applicability of the Mayo method for determining transfer constants. They concluded that transfer constants should be slightly overestimated by the Mayo method with the discrepancy being $<3\%$.[20]

The effect of chain length dependent termination on the ln CLD method can be calculated numerically. The form of chain length dependent termination is such that termination occurs mainly by the interaction of long (relatively immobile) chains with shorter (mobile) chains. A consequence of this is that the molecular weight distribution of chains formed by combination will resemble that of the chains formed by disproportionation and the major part of the molecular weight distribution can be represented by an exponential. The net effect will be to remove the effects of combination in causing nonlinearity of the ln CLD plot for high molecular weights (significantly above the entanglement limit).

Effects of Choice of Baseline and Integration Limits on the ln Chain Length Distribution and the Values of Measured Transfer Constants

The baseline and integration limits are very important parameters for a successful GPC analysis. Noise levels in GPC traces of 1–2% are not uncommon; these, along with baseline artifacts, complicate an accurate definition of the baseline either in terms of the exact level or the start/end of the peak.

The effect of a baseline offset of 1% of the maximum peak height in the GPC trace on the derived ln CLD

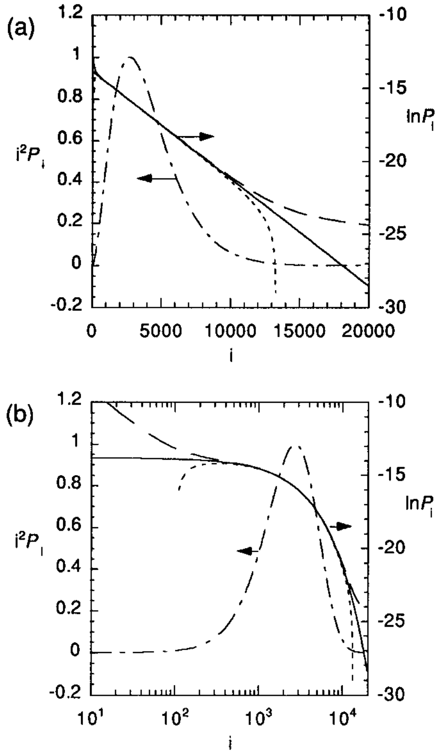

Figure 4. Calculated GPC trace for polymerization with termination by disproportionation/chain transfer (– • –). ln CLD plot after applying baseline offsets to the original GPC trace: no offset (—), 1% offset (– – –) and −1% offset (- - -). Graph of (a) linear *x*-axis (b) log *x*-axis.

Table 1. Effect of Baseline Choice on GPC Molecular Weights and Polydispersities[a]

baseline offset, %	slope[a]	$\bar{X}_n$			$\bar{X}_w$	$\bar{X}_w/\bar{X}_n$	
		slope[b]	integration				
0	−0.000 730	1370	1370[c]	1480[d]	2740[d]	2.00[c]	1.85[d]
1	−0.000 725	1379		1416[d]	2741[d]		1.94[d]
−1	−0.000 736	1359		1553[d]	2739[d]		1.76[d]

[a] Simulated chain length distribution calculated by applying eq 8 with $S = 0.999\,27$. [b] Slope determined for region with intensity >10% of maximum peak height in the GPC trace. [c] Degree of polymerization obtained by integration, applying eq 25 or 26 with limits of 1 and ∞. [d] Degree of polymerization obtained by integration, applying eq 25 or 26; limits set by taking that part of the "GPC trace" (i^2P_i *vs* i) where the signal intensity exceeds 1% of maximum peak height.

plot is shown in Figure 4. The extremities of the ln CLD plot diverge from the desired straight line. However, over the region coinciding with the peak of the untransformed GPC distribution, the slope is essentially unaffected (see Table 1). The value is within ±1% of the true value.

On the other hand, if the molecular weight averages are derived by integration of the GPC trace (eqs 25 and 26), the effect of a 1% baseline offset on the value of $\bar{X}_n$ is *ca.* 7%. There is, however, essentially no effect on $\bar{X}_w$. Calculated polydispersities are, therefore, significantly less than the actual values (see Table 1); the lesser effect on $\bar{X}_w$ is due to this number being more sensitive to the high molecular weight end of the distribution, which is better defined. There is a logarithmic relationship between elution volume and chain length; thus P_i is proportional to (detector response)/(chain length)^2 for a refractive index or other concentration-sensitive detector.[14,23−25]

$$\bar{X}_n = \frac{\sum_{i=1}^{\infty} iP_i}{\sum_{i=1}^{\infty} P_i} \tag{25}$$

$$\bar{X}_w = \frac{\sum_{i=1}^{\infty} i^2P_i}{\sum_{i=1}^{\infty} iP_i} \tag{26}$$

Thus, in practice, the direct use of eq 21 (*i.e.* obtaining slope as $i \to \infty$) is not recommended for transfer constant measurements. It is better to obtain the slope near the peak signal of the untransformed chromatogram. It also follows that, for systems where the termination mechanism is established as being largely by transfer or disproportionation, the appearance of the ln CLD plot might be used to assess the quality of baseline selection in GPC.

Example. Chain length distributions have been simulated for the bulk polymerization of methyl methacrylate carried out in the presence of a methyl methacrylate macromonomer (T, $\bar{X}_n = 24$, $\bar{X}_w/\bar{X}_n = 1.3$) with [2,2′-azobis(2,4-dimethylpentanenitrile)] = 1.9×10^{-3} M as initiator at 45 °C (see the accompanying paper).[26] The experimental C_T for the macromonomer in MMA polymerization is 0.18_{45}. Conversions for the experimental polymerizations were <10%. The simulations were carried for values of [T]/[M] and $k_{tc}/(k_{tc} + k_{td})$ shown in Table 2. For each value of $k_{tc}/(k_{tc} + k_{td})$, the value of S was chosen to give the same value of $\bar{X}_n$. The value of $\bar{X}_n$ with no added transfer agent was chosen to be similar to the experimental $\bar{X}_n$.

To achieve this, the chain length of propagating species involved in termination (ν) was chosen according to the following expression:

$$\nu = \bar{X}_n(\text{desired})\left(\frac{2 - \dfrac{k_{tc}}{k_{tc} + k_{td}}}{2}\right)$$

The experimental and calculated molecular weight data are summarized in Table 2. The transfer constants derived from analysis of these datasets are shown in Table 3. The slopes of the ln CLD plots were determined over ranges corresponding to the top 20% and last 10% of the signal intensity of the relevant GPC trace (i^2P_i plot), and these are shown in Figure 5. For values of $k_{tc}/(k_{tc} + k_{td}) > 0.0$, the ln CLD plot is not linear and the slope values are therefore strongly dependent on the *x*-axis range over which they are determined. The "top 20%" slopes (see Figure 5) are significantly different from the limiting slope [*i.e.* ln S = slope for $k_{tc}/(k_{tc} + k_{td}) = 0.0$]; however, the transfer constants derived from the slope *vs* [T]/[M] plot are not substantially affected (<10% for worst case where $k_{tc}/(k_{tc} + k_{td}) = 1.0$, reducing to <1% where $k_{tc}/(k_{tc} + k_{td}) \leq 0.5$; see Table 3). Inclusion of chain length dependent termination in our model would further reduce the predicted error (see above). Thus, for signal to noise and baseline selection considerations (see above), it is recommended that the slopes used in the conjunction with the ln CLD method be taken over the region

Table 2. Experimental and Calculated Molecular Weight Data[a]

			$\bar{X}_n$ for $\frac{k_{tc}}{k_{tc}+k_{td}}$			$\bar{X}_w/\bar{X}_n$ for $\frac{k_{tc}}{k_{tc}+k_{td}}$ [c]		
$[T]/[M] \times 10^3$	expl $\bar{X}_n$[b]	$\bar{X}_w/\bar{X}_n$	0	0.5	1.0	0	0.5	1.0
0	5153	1.85	5155	5155	5156	2.00	1.87	1.50
0.8837	2985	1.81	2802	2802	2802	2.00	1.95	1.75
1.7590	2158	1.74	1930	1930	1930	2.00	1.97	1.85
2.7440	1677	1.68	1429	1429	1429	2.00	1.98	1.90

[a] Experimental data is for polymerization of methyl methacrylate carried out in the presence of a methyl methacrylate macromonomer (T, $\bar{X}_n = 24$, $\bar{X}_w/\bar{X}_n = 1.3$) with [2,2′-azobis(2,4-dimethylpentanenitrile)] = 1.9×10^{-3} M as initiator at 45 °C.[26] [b] Experimental degree of polymerization. All numbers are rounded to the nearest integer. [c] Based on chain length distributions calculated using eq 23. Degrees of polymerization obtained by integration, applying eq 25 or 26 with limits of 1 and ∞.

Table 3. Experimental and Calculated Transfer Constants

		calculated C_T for $\frac{k_{tc}}{k_{tc}+k_{td}}$ [a]		
method	expl C_T	0	0.5	1.0
Mayo	0.14_7[b] (0.18_2)[c]	0.184	0.184	0.184
ln CLD (top 20%)[d]	0.18_{45}[e]	0.184	0.182	0.169
ln CLD (last 10%)[f]		0.184	0.181	0.180

[a] Based on chain length distributions calculated using eq 23. [b] Experimental transfer constant obtained by application of the conventional Mayo method (eq 13) and experimental $\bar{X}_n$ (see Table 2). [c] Experimental transfer constant obtained by application of the conventional Mayo method (eq 13) and values of $\bar{X}_n$ estimated by assuming $\bar{X}_n = \bar{X}_w/2.0$ (see the text). [d] Slopes taken for top 20% of "GPC distribution". [e] Experimental transfer constant obtained by application of the ln CLD method (see the accompanying paper).[26] [f] Slopes taken for last 10% of "GPC distribution".

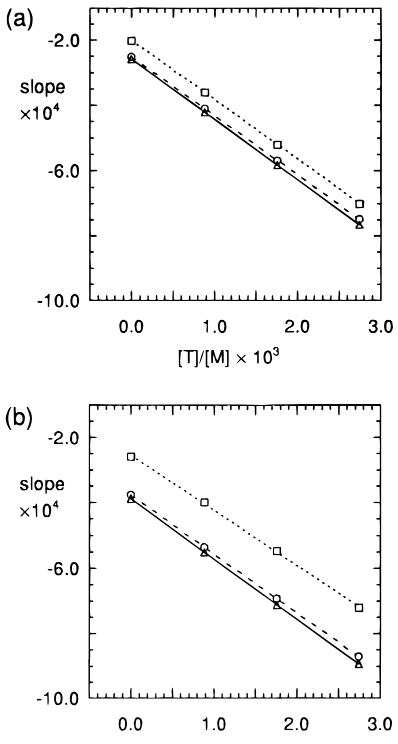

Figure 5. "Mayo plots" in which the calculated limiting slopes (triangles, —), "last 10% slopes" (circles, — — —), and "top 20% slopes" (squares, - - -) are graphed as a function of [T]/[M]. Graph of (a) $k_{tc}/(k_{tc} + k_{td}) = 0.5$ and (b) $k_{tc}/(k_{tc} + k_{td}) = 1.0$. Data are for systems reported in Tables 2 and 3.

corresponding to maximum intensity of the GPC trace rather than over the tail of the distribution.

It should also be noted that the polydispersities calculated for reasonable values of $k_{tc}/(k_{tc} + k_{td})$ are significantly higher than the experimental values (for MMA polymerization, the value of $k_{tc}/(k_{tc} + k_{td})$ is generally believed to be ≤ 0.5[18,19]). One possible explanation for lower than expected polydispersities is the effect of baseline choice, as mentioned above. A truncation of the baseline at low molecular weights is likely because of the use of a macromonomer transfer agent. If it is assumed that this is the case, then a more accurate value of $\bar{X}_n$ may be obtained by using the approximation $\bar{X}_n = \bar{X}_w/2.0$ (a reasonable assumption if termination is largely by chain transfer or disproportionation).[27] The transfer constant obtained using the corrected $\bar{X}_n$ values is 0.182, which is in excellent agreement with the value obtained by the ln CLD method.

Polydispersity data for chain transfer experiments commonly are not reported in the literature, even where GPC was used to obtain $\bar{M}_n$. However, polydispersities of 1.6−1.8 appear typical where reported.[28−30] This narrowing of the molecular weight distribution has been attributed[30] to the fact that polydispersities are expected to narrow with decreasing molecular weight and lower S according to the relationship $\bar{X}_w/\bar{X}_n = 1 + S$ if termination is by disproportionation or chain transfer.[9] However, this explanation is unlikely for polymers of the molecular weights reported in the present[26] or other works[28−30] as the effect on polydispersity should be less than 5% for $\bar{X}_n > 10$ and less than 0.5% for $\bar{X}_n > 100$.[27] It is more likely that narrow polydispersities (<2.0) seen in low-conversion polymerizations carried out in the presence of chain transfer agents are caused by baseline selection problems. Some transfer constant data obtained by the Mayo analysis of GPC data should be reevaluated in this light. However, caution would be required since application of a $\bar{X}_w/\bar{X}_n = 2.0$ correction assumes (i) low-conversion data and (ii) that there are no mechanisms that lead to chain distribution narrowing. Narrow polydispersities can arise if there is significant termination by combination, if living behavior is exhibited,[31,32] or if the polymer has been inadvertently fractionated prior to characterization.

Conclusions

Analysis of ln chain length distributions can offer substantial benefits in accuracy and precision over the conventional Mayo analysis when determining transfer constants by analysis of GPC data.

The basis of this method has been examined in terms of classical statistics and with the aid of simulated chain length distributions. One major benefit is that the requisite information can be obtained by analysis of a small segment of the chain length distribution. This means that it may be applied under circumstances where there may be overlap between the distributions of the new polymer being formed and the transfer agent (*i.e.* transfer constants to polymeric species can be determined).

The method also has general application, since it is less sensitive to the presence of artifacts in GPC traces caused by experimental noise or poor baseline selection. Transfer constants appear generally insensitive to details of the mechanism of radical−radical termination (whether termination is by combination or disproportionation and whether termination is chain length dependent or not).

It is proposed that greatest accuracy will be obtained by analysis of that part of the $\log_e$ chain length distribution which corresponds to the maximum intensity in the "GPC" molecular weight distribution.

The scope for obtaining mechanistic information on termination mechanisms by analysis of molecular weight distributions of low-conversion polymers is limited by our currently poor understanding of the effects of chain length dependent termination of such distributions. This problem will be addressed in future work.

Acknowledgment. We wish to acknowledge Tom Spurling, Matt Ballard, and Mark Deady for giving us confidence in our derivations and for helpful discussions. We also acknowledge Bob Gilbert (University of Sydney) for promoting the benefits of the ln CLD method for transfer constant determination.

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MA960851K