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Comparison of the Mayo and Chain Length Distribution Procedures for the Measurement of Chain Transfer Constants

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ABSTRACT: The Mayo and chain length distribution (CLD) procedures for the measurement of chain transfer constants are outlined and compared, and it is found that both procedures are essentially equivalent and yield reliable results. It is shown that both procedures are relatively insensitive to changes in initiator concentration under practical circumstances and that the most reliable results are obtained with the Mayo procedure using the weight-average molecular weight and with the CLD procedure using the slope in the ln(number distribution) at the peak molecular weight. The CLD procedure is discussed in more detail, and it is shown that as long as termination is not a significant chain stopping event, the ln(number distribution) should be a straight line. Therefore, the limiting slope of such a plot can be reliably obtained, preferably from the peak molecular weight region, as previously discussed by Moad and Moad [*Macromolecules* **1996**, *29*, 7727]. However, when termination is significant, the limiting slope is only reached at high molecular weights, and it is unlikely that such slopes can be reliably obtained from experiments.

Introduction

In recent years there has been renewed interest in developing methods for the determination of chain transfer constants. One of the reasons for this is likely to be the growing interest in (controlled) production of low molecular weight polymers, for example to be used in high solids coatings. In this regard the use of catalytic chain transfer agents is attracting considerable attention.[1−6]

The general chain transfer constant, *C*, is defined as the ratio of the chain transfer and propagation rate coefficients, k_{tr}/k_p. For example, C_S is the ratio of the rate coefficient for chain transfer to chain transfer agent S and the rate coefficient for propagation, and it is a measure of the reactivity of a chain transfer agent. The higher is C_S, the lower the concentration of chain transfer agent required for a particular molecular weight reduction.[7,8] This effect on the molecular weight of the polymer is quantitatively given by the Mayo equation, which expresses the reciprocal of DP_n, the number-average degree of polymerization, as a function of the rates of chain growth and chain stopping:[7,9]

$$\frac{1}{DP_n} = \frac{(1+\lambda)\langle k_t\rangle[R^\bullet]}{k_p[M]} + C_M + C_S\frac{[S]}{[M]} \qquad (1)$$

In this expression, λ is the fraction of termination by disproportionation, $\langle k_t\rangle$ the average termination rate coefficient, $[R^\bullet]$ the overall radical concentration, [M] the monomer concentration, C_M the chain transfer constant for chain transfer to monomer, and [S] the concentration of chain transfer agent. This expression is based on overall chain growth and chain stopping rates, and the only assumption regarding reaction mechanisms is that the overall kinetic scheme is complete. The steady state and so-called long-chain approximations are also made in deriving eq 1, but otherwise this expression is *exact*.

The usual procedure for measuring the chain transfer constant C_S—henceforth referred to as the Mayo procedure—involves the determination of the average degree of polymerization for a range of [S]/[M] values and plotting the data as DP_n^{-1} vs [S]/[M], i.e., a so-called Mayo plot.[7,9] The value of C_S is then determined as the straight-line slope of this plot. This procedure assumes that the product $\langle k_t\rangle[R^\bullet]$ is independent of variation of [S]/[M]. However, if termination is chain length dependent in rate, then $\langle k_t\rangle[R^\bullet]$ will vary with [S]/[M] as the average degree of polymerization varies and hence the frequency of termination varies,[10−12] even if the initiator concentration remains constant. This implies that the first term on the rhs of eq 1 is in general not a constant, and so a Mayo plot need not necessarily be linear. In principle, this is a weakness of the Mayo method for determining C_S. However, in practice, this effect does not seem to be significant, which suggests that, in systems with added chain transfer agent, the first term on the rhs of eq 1 generally makes a negligible contribution to DP_n^{-1}.

A more recent procedure for determining C_S has been developed by Gilbert and co-workers.[13−16] This procedure is based upon taking the high molecular weight slope of the number molecular weight distribution, *P*(*M*), plotted as ln(*P*(*M*)) vs *M*, a type of plot which we will henceforth call a ln *P* plot. The high molecular weight slope of this plot, denoted as Λ_{high} in the remainder of

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this paper, is defined and related to kinetic parameters, respectively, as follows:[14]

$$\Lambda_{\mathrm{high}} = \lim_{M\to\infty} \frac{\mathrm{d}\ln(P(M))}{\mathrm{d}M} = -\left(\frac{\langle k_{\mathrm{t}}\rangle[\mathrm{R}^\bullet]}{k_{\mathrm{p}}[\mathrm{M}]} + C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]}\right)\frac{1}{m_0} \quad (2a)$$

Here m_0 is the mass of the monomer. Equation 2a may alternatively be written in terms of chain length i: we denote $\Lambda(i)$ as the slope of a plot of $\ln(P(i))$ vs i and have

$$\Lambda(\mathrm{high}) = \lim_{i\to\infty} \frac{\mathrm{d}\ln(P(i))}{\mathrm{d}i} = -\left(\frac{\langle k_{\mathrm{t}}\rangle[\mathrm{R}^\bullet]}{k_{\mathrm{p}}[\mathrm{M}]} + C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]}\right) \quad (2b)$$

We have chosen to denote these slopes in the same way—Λ_{M} for a $\ln(P(M))$ plot and $\Lambda(i)$ for a $\ln(P(i))$ plot—because in essence they are the same quantity, even if, as indicated, they differ formally by a factor of m_0, due to the chain length i being defined as M/m_0. In experiments one normally works with $\ln(P(M))$, in which event the determination of C_{S} involves the measurement of Λ_{high} as a function of [S]/[M] and then plotting $-\Lambda_{\mathrm{high}} m_0 = -\Lambda(\mathrm{high})$ vs [S]/[M], a type of plot which will be called a CLD plot in the remainder of this paper. According to eq 2, C_{S} is equal to the straight line slope of a CLD plot. This procedure for determining C_{S} we will refer to as the CLD procedure.

Since in each type of plot the ordinates are ostensibly different ($\mathrm{DP}_{\mathrm{n}}^{-1}$ for Mayo plots as opposed to Λ(high) for CLD plots), one might obtain the impression that the two methods for determining C_{S} are distinct. That this is not so is immediately obvious from the similarity of eqs 1 and 2. In fact, the issue is really how the Mayo and CLD procedures are different, because the only difference between eqs 1 and 2 is that the termination term in the latter does not depend on the fraction of termination by disproportionation. So it may be said that both procedures should yield very similar results. However, it has been a contentious issue in the literature as to which procedure in general yields more reliable results.[3,5,15−22] A general misconception seems to be that the use of eq 2 eliminates any effect of chain-length-dependent termination, as such effects become negligible in the high molecular weight region of the molecular weight distribution, and that therefore using eq 2 should always be the procedure of choice. However, eq 2 contains exactly the same kinetic parameters as eq 1, so if chain-length-dependent effects are important, it is conceivable that these effects are similar in both procedures. Since the termination term in both expressions is the one most prone to chain length effects, it must be this term that is decisive in determining the reliability of the two procedures.

In what follows we determine the practical effect of this termination term on the apparent chain transfer constant for *n*-dodecanethiol in methyl methacrylate at 40 and 60 °C. We do this by varying the initiator concentration over 4 orders of magnitude. Subsequently, we will discuss the CLD procedure in some detail as we feel that some of its advantages and disadvantages have not received sufficient attention in the literature. In particular, we will consider the issue of how to obtain reliable values of Λ(high) from experimental results, including whether or not this is likely to be possible. Finally, the two procedures will be compared, and an attempt will be made to identify practical situations in which these procedures are most useful.

Experimental Section

Materials. Methyl methacrylate (MMA; Aldrich, 99%) was passed through a column of activated basic alumina (ACROS, 50−200 μm) in order to remove inhibitor, *n*-dodecanethiol (DDM; Aldrich, 98%) was used without further purification, and 2,2′-azobis(isobutyronitrile) (AIBN; DuPont) was recrystallized twice from methanol and used as initiator.

General Polymerization Procedure. A stock solution of ~650 mg of AIBN in ~40 mL of methyl methacrylate was prepared from which four samples of ~5 mL were transferred into glass ampules (all quantities were accurately weighed). To each of these solutions was added a varying amount of dodecanethiol (ranging roughly from 20 to 100 mg), and the solutions were subsequently purged with high-purity nitrogen gas (BOC gases) for 10 min. The ampules were subsequently sealed with rubber septa and placed in a thermostated water bath (40 and 60 °C). From the remainder of the initiator stock solution ~4 mL was diluted with ~36 mL of methyl methacrylate after which four new reaction ampules were prepared. The third initiator solution was prepared from a further 10-fold dilution, after which the final initiator solution was prepared by a 20-fold dilution of the third initiator solution. Polymerizations were restricted to low conversions, with reaction mixtures being quenched by rapid cooling and addition of hydroquinone prior to gravimetric determination of final conversions.

Molecular Weight Analyses. Molecular weight distributions were determined by size exclusion chromatography using a GBC Instruments LC1120 HPLC pump, a Shimadzu SIL-10A autoinjector, a column set consisting of a Polymer Laboratories 3.0 μm bead-size guard column (50 × 7.5 mm) followed by four linear PL columns (10^6, 10^5, 10^4, and 10^3), and a VISCOTEK dual detector model 250 differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as eluent at 1 mL/min. Calibration of the SEC equipment was performed with narrow poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range 200−1.6×10^6 g mol^{-1}). Number molecular weight distributions were obtained from the SEC results in the standard fashion.[14]

Results and Discussion

The measurement of the chain transfer constant to a chain transfer agent involves the measurement of a particular property of the molecular weight distribution as a function of the ratio of chain transfer agent and monomer concentrations (i.e., [S]/[M]), irrespective of whether eq 1 or eq 2 is used. Typical molecular weight distributions obtained in our current studies are shown in Figure 1. It can be seen that the molecular weight distributions are congruent with distributions expected from a chain transfer dominated low-conversion free-radical polymerization; also as expected, the molecular weight distributions shift to lower molecular weights with increasing chain transfer agent concentrations.

Chain Transfer Constants from the Mayo Procedure. First, the average degree of polymerization obtained from these molecular weight distributions was used to determine C_{S} according to eq 1. The number-average degree of polymerization can be obtained directly from the *number*-average molecular weight, M_{n}, by dividing M_{n} by the mass of the monomer, m_0. Although this procedure is in principle the only correct procedure to determine DP_{n} from a molecular weight distribution, in practice this procedure has an important shortcoming. The number-average molecular weight is very sensitive to errors in the analysis of the size exclusion chromatogram (e.g., peak and baseline selec-

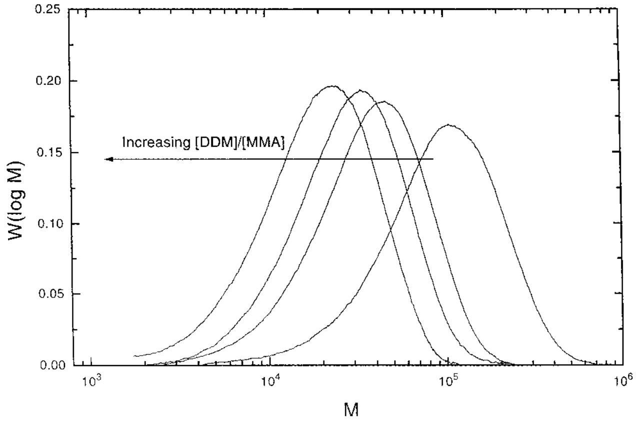

Figure 1. Molecular weight distributions obtained in the experiment for the determination of the chain transfer constant of *n*-dodecanethiol in methyl methacrylate at 40 °C.

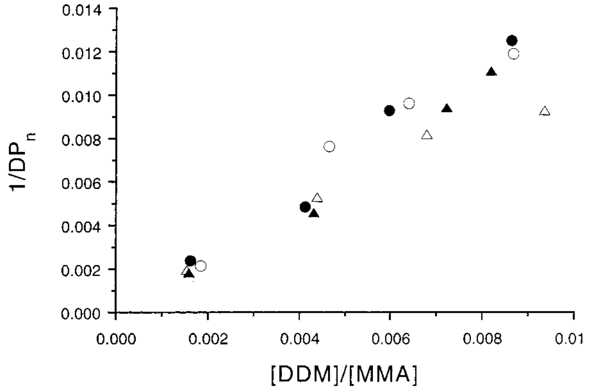

Figure 2. Mayo plots for the determination of the chain transfer constant of *n*-dodecanethiol in methyl methacrylate at 60 °C based upon $DP_n = M_n/100.12$: (●) [AIBN] = 1.0 × 10^{-1} M, (○) [AIBN] = 1.0 × 10^{-2} M, (▲) [AIBN] = 1.2 × 10^{-3} M, (△) [AIBN] = 5.0 × 10^{-5} M.

tion), and this often leads to scattered results.[5,19] This is especially the case for low-molecular-weight polymers. An alternative procedure for obtaining DP_n from a molecular weight distribution is from the *weight*-average molecular weight, M_w. In a chain-transfer-dominated system, M_w is equal to $2M_n$ (except for very low molecular weights), and hence $DP_n = M_w/(2m_0)$ for such systems. The use of M_w is often more reliable, because M_w is much less sensitive to errors in analysis of the size-exclusion chromatogram, as has been previously discussed in great detail.[5,19,23,24] In the present study we used both M_n and M_w in the analyses.

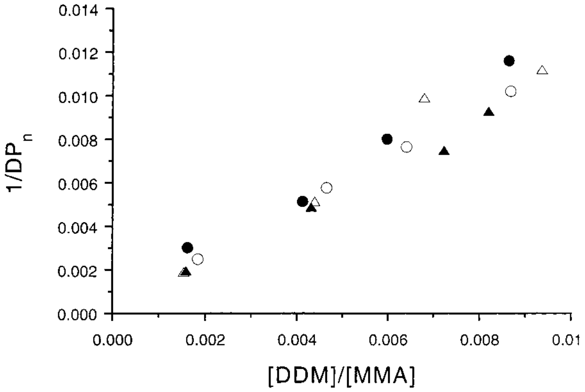

Figure 3. Mayo plots for the determination of the chain transfer constant of *n*-dodecanethiol in methyl methacrylate at 60 °C based upon $DP_n = M_w/(2 \times 100.12)$: (●) [AIBN] = 1.0 × 10^{-1} M, (○) [AIBN] = 1.0 × 10^{-2} M, (▲) [AIBN] = 1.2 × 10^{-3} M, (△) [AIBN] = 5.0 × 10^{-5} M.

Table 1. Summary of Experimental Results at 40 °C Relevant for the Mayo Procedure

[AIBN][a]	[DDM]/[MMA][b]	M_n[c]	M_w[d]	conv[e]
9.2 × 10^{-2}	1.74	42.0	78.9	7.0
	2.87	32.1	56.0	5.4
	5.39	21.7	36.6	4.8
	9.28	13.1	22.9	6.8
		$C_S = 0.70$	$C_S = 0.82$	
9.2 × 10^{-3}	1.70	64.0	117.8	3.4
	4.80	27.2	46.0	3.8
	6.76	21.3	35.0	4.4
	9.77	13.8	23.4	3.9
		$C_S = 0.69$	$C_S = 0.84$	
9.3 × 10^{-4}	1.54	73.4	135.1	4.6
	4.91	26.0	46.0	4.5
	6.44	20.0	36.0	4.9
	10.56	12.4	22.0	5.0
		$C_S = 0.75$	$C_S = 0.85$	
4.7 × 10^{-5}	1.95	50.2	107.3	0.9
	5.26	24.7	44.3	0.9
	7.10	17.5	32.4	0.6
	10.05	14.4	24.6	0.5
		$C_S = 0.63$	$C_S = 0.78$	

[a] Initiator concentration (mol dm^{-3}). [b] Ratio of dodecanethiol and monomer concentrations (10^{-3}). [c] Number-average molecular weight (10^3 g mol^{-1}). [d] Weight-average molecular weight (10^3 g mol^{-1}). [e] Final conversion (%).

As already stated in the Introduction, the most likely parameter to cause possible problems using the Mayo procedure is the termination term in eq 1. This term can be controlled by the overall radical concentration, which in turn is controlled by the initiator concentration and temperature. In the present studies the initiator concentration was varied from ~1 × 10^{-1} to ~5 × 10^{-5} M, which corresponds roughly to about a 10 times larger and 200 times smaller concentration than is commonly used in this type of experiment (i.e., ~1 × 10^{-2} M). These experiments were carried out at 40 and 60 °C, at which the decomposition rate coefficient of AIBN changes from ~5 × 10^{-7} to ~1 × 10^{-5} s^{-1}.[25] In Figures 2 and 3, Mayo plots based on M_n and M_w, respectively, are presented for experiments using different initiator concentrations at 60 °C. When comparing these figures, it can be seen that the data in Figure 2, which are based on M_n, are slightly more scattered than those in Figure 3, which are based upon M_w. However, in neither figure can significant changes in the Mayo plots be observed for different initiator concentrations. This is further demonstrated by the chain transfer constants obtained from these plots and which are listed in Tables 1 and 2 for 40 and 60 °C, respectively.

The results presented in Figures 2 and 3 and Tables 1 and 2 clearly show the invariance of the obtained chain transfer constant to changes in the initiator concentration; observed differences are within experimental error. Overall, the chain transfer constants based upon M_n are in satisfactory agreement with those obtained using $M_w/2$. However, the results based upon M_n show a larger scatter than those based upon $M_w/2$, which is in accordance with the expectation that M_w can be determined more reliably than M_n.

Chain Transfer Constants from the CLD Procedure. The CLD procedure is based upon the use of eq 2 which indicates that the slope of a ln *P* plot in the high molecular weight limit is a simple function of the fundamental kinetic parameters of a system. Although this expression is only valid for very high molecular

Table 2. Summary of Experimental Results at 60 °C Relevant for the Mayo Procedure

[AIBN][a]	[DDM]/[MMA][b]	M_n[c]	M_w[d]	conv[e]
1.0×10^{-1}	1.62	42.2	66.1	3.1
	4.12	20.7	38.9	2.5
	5.97	10.8	25.0	2.7
	8.63	8.0	17.3	2.5
		$C_S = 1.51$	$C_S = 1.24$	
1.0×10^{-2}	1.84	46.5	80.5	1.3
	4.64	13.1	34.8	1.0
	6.40	10.4	26.2	1.1
	8.67	8.4	19.6	1.3
		$C_S = 1.43$	$C_S = 1.13$	
1.2×10^{-3}	1.59	54.7	102.9	1.6
	4.31	21.9	40.9	1.4
	7.22	10.6	26.7	1.5
	8.19	9.0	21.6	1.2
		$C_S = 1.42$	$C_S = 1.06$	
5.0×10^{-5}	1.54	51.4	105.5	0.4
	4.38	18.9	38.9	0.1
	6.79	12.2	20.2	0.1
	9.385	10.8	17.8	0.1
		$C_S = 0.97$	$C_S = 1.27$	

[a] Initiator concentration (mol dm^{-3}). [b] Ratio of dodecanethiol and monomer concentrations (10^{-3}). [c] Number-average molecular weight (10^3 g mol^{-1}). [d] Weight-average molecular weight (10^3 g mol^{-1}). [e] Final conversion (%).

weights (vide infra), Moad and Moad[19] showed the complete equivalence of the Mayo and CLD procedures in chain-transfer-dominated systems. They indicated that in such systems ln *P* plots should, in principle, be straight from low to very high molecular weights, implying that the slope can be taken over any region of a ln *P* plot and used for accurate determination of chain transfer constants. Of course, the region of the molecular weight distribution that is most likely to give reliable results is the region where the detector response is highest, i.e., the peak molecular weight of the size-exclusion chromatogram.[19] It was therefore recommended[19] that, for systems completely dominated by chain transfer, most reliable values of C_S will be obtained if the value of Λ_{high} is taken as the slope of a ln *P* plot in the region of the peak molecular weight of the SEC distribution (as opposed to the slope in a region of genuinely "high" molecular weight). This recommendation has been substantiated by several different experimental studies.[3,5,19,21,26−28]

As illustrated in Figure 4, here we will use three different regions to take the slope in a $\ln(P(M))$ plot: (1) a very high molecular weight region between A and B, (2) a peak molecular weight region which starts between M_n and M_w and finishes between M_z and M_{z+1}, and (3) a high molecular weight region between the peak molecular weight and B. The corresponding slopes will be denoted by Λ_{high} (Λ(high) for a $\ln(P(i))$ plot), Λ_{peak} (Λ(peak)), and Λ_{full} (Λ(full)), respectively. In Figures 5−7, CLD plots are shown based on these three slopes for a range of initiator concentrations at 60 °C. As in the case of the Mayo procedure, no significant effect of the used initiator concentration on the CLD plots is observed. Furthermore, the three figures are nearly identical, a consequence of the linearity of the ln *P* plots (i.e., $\Lambda_{high} \approx \Lambda_{peak} \approx \Lambda_{full}$), as expected for a system dominated by chain transfer.[19] This is seen even more clearly in Tables 3 and 4, where all the slopes and chain transfer constants are listed. Comparison of the chain transfer constants listed in Tables 3 and 4 with the corresponding values in Tables 1 and 2 shows that the values obtained by the CLD procedure compare best with those from the Mayo procedure using $M_w/2$. This is in accordance with earlier studies.

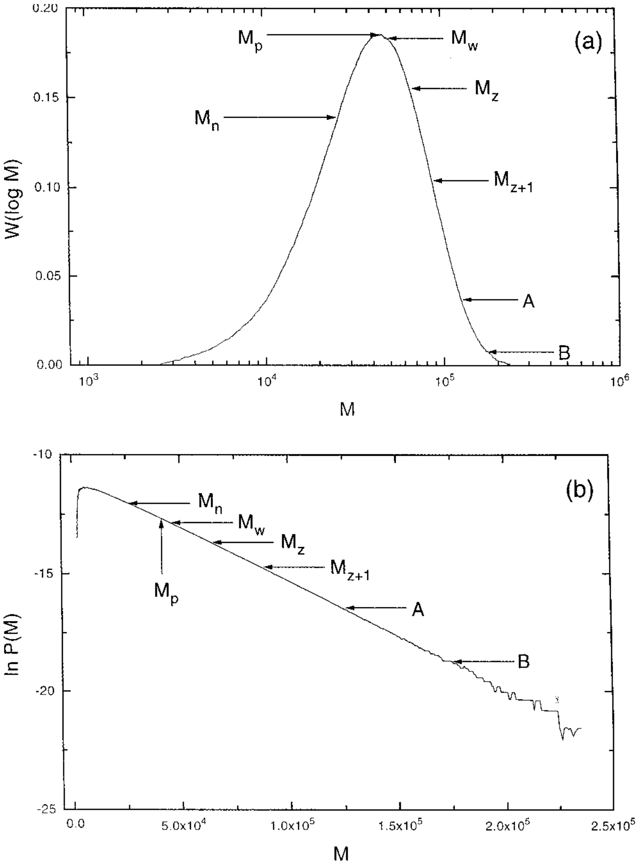

Figure 4. A typical molecular weight distribution plotted as (a) $w(\log(M))$ vs $\log(M)$ and (b) $\ln(P(M))$ vs M. The positions of the most important molecular weight averages and the position where Λ_{high} is determined (A → B) are indicated.

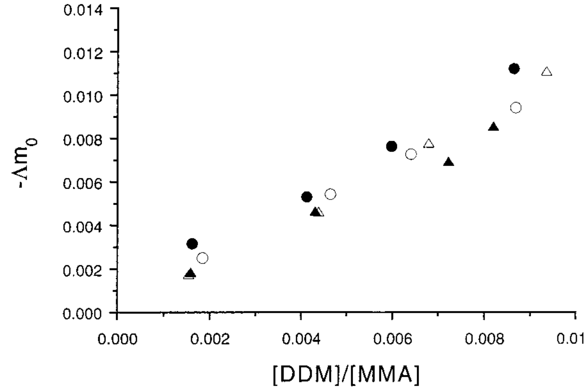

Figure 5. CLD plots for the determination of the chain transfer constant of *n*-dodecanethiol in methyl methacrylate at 60 °C based upon $\Lambda = \Lambda_{high}$: (●) [AIBN] = 1.0×10^{-1} M, (○) [AIBN] = 1.0×10^{-2} M, (▲) [AIBN] = 1.2×10^{-3} M, (△) [AIBN] = 5.0×10^{-5} M.

In summary, it can be concluded that both the Mayo and CLD procedures are suitable and robust for the determination of C_S values under our experimental conditions. In particular, neither method is significantly affected by changing initiator concentration; i.e., any possible chain-length dependence of the termination reaction is not significantly affecting the results of either method. We are confident that our findings hold for transfer-agent-dominated systems in general, because every indication is that our experimental systems

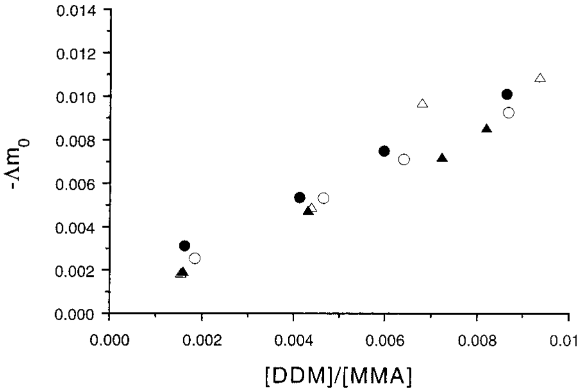

Figure 6. CLD plots for the determination of the chain transfer constant of *n*-dodecanethiol in methyl methacrylate at 60 °C based upon $\Lambda = \Lambda_{peak}$: (●) [AIBN] = 1.0×10^{-1} M, (○) [AIBN] = 1.0×10^{-2} M, (▲) [AIBN] = 1.2×10^{-3} M, (△) [AIBN] = 5.0×10^{-5} M.

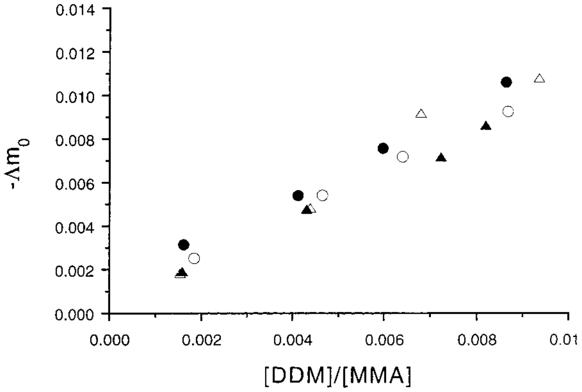

Figure 7. CLD plots for the determination of the chain transfer constant of *n*-dodecanethiol in methyl methacrylate at 60 °C based upon $\Lambda = \Lambda_{full}$: (●) [AIBN] = 1.0×10^{-1} M, (○) [AIBN] = 1.0×10^{-2} M, (▲) [AIBN] = 1.2×10^{-3} M, (△) [AIBN] = 5.0×10^{-5} M.

(AIBN-initiated polymerization of MMA in the presence of DDM at 40 and 60 °C) are typical transfer-dominated systems.

Discussion of Chain Transfer Constant Values. Comparison of the chain transfer constants obtained at the two different temperatures clearly shows a significant increase in C_S from about 0.8 at 40 °C to 1.1 at 60 °C. These results are consistent with other results obtained in our group[27] but are different from the results obtained by Hutchinson et al.,[17] who measured a constant C_S of 0.68 over the temperature range 20−80 °C for MMA/DDM. These authors also used the CLD procedure, but their experiments employed pulsed-laser-induced initiation rather than continuous initiation, as used here. This is relevant because eqs 1 and 2 are only valid under steady-state conditions. It therefore seems probable that for MMA/DDM C_S does in fact have a small, positive activation energy; i.e., the activation energy for k_{tr} exceeds the activation energy for k_p by about 10 kJ mol^{-1}.[27]

Table 3. Summary of Experimental Results at 40 °C Relevant for the CLD Procedure

[AIBN][a]	[DDM]/[MMA][b]	Λ_{high}[c]	Λ_{peak}[d]	Λ_{full}[e]
9.2×10^{-2}	1.74	−2.48	−2.65	−2.55
	2.87	−3.79	−3.62	−3.75
	5.39	−5.81	−5.65	−5.73
	9.28	−8.93	−8.80	−8.92
		$C_S = 0.84$	$C_S = 0.81$	$C_S = 0.83$
9.2×10^{-3}	1.70	−1.62	−1.75	−1.68
	4.80	−4.67	−4.48	−4.59
	6.76	−6.19	−6.03	−6.13
	9.77	−8.92	−8.52	−8.73
		$C_S = 0.90$	$C_S = 0.84$	$C_S = 0.87$
9.3×10^{-4}	1.54	−1.44	−1.51	−1.45
	4.91	−4.55	−4.36	−4.47
	6.44	−5.92	−5.54	−5.74
	10.56	−9.32	−8.89	−9.12
		$C_S = 0.87$	$C_S = 0.82$	$C_S = 0.85$
4.7×10^{-5}	1.95	−1.74	−1.85	−1.80
	5.26	−4.76	−4.54	−4.66
	7.10	−6.36	−6.01	−6.20
	10.05	−8.44	−8.25	−8.38
		$C_S = 0.83$	$C_S = 0.79$	$C_S = 0.82$

[a] Initiator concentration (mol dm^{-3}). [b] Ratio of dodecanethiol and monomer concentrations (10^{-3}). [c] Slope of ln($P(M)$) vs M in high molecular weight region (10^{-5}, see text). [d] Slope of ln($P(M)$) vs M in peak molecular weight region (10^{-5}, see text). [e] Slope of ln($P(M)$) vs M taken from peak to high molecular weight (10^{-5}, see text).

Table 4. Summary of Experimental Results at 60 °C Relevant for the CLD Procedure

[AIBN][a]	[DDM]/[MMA][b]	Λ_{high}[c]	Λ_{peak}[d]	Λ_{full}[e]
1.0×10^{-1}	1.62	−3.16	−3.12	−3.14
	4.12	−5.31	−5.35	−5.39
	5.97	−7.64	−7.50	−7.56
	8.63	−11.2	−10.1	−10.6
		$C_S = 1.16$	$C_S = 1.01$	$C_S = 1.08$
1.0×10^{-2}	1.84	−2.51	−2.55	−2.52
	4.64	−5.43	−5.33	−5.41
	6.40	−7.27	−7.11	−7.18
	8.67	−9.40	−9.27	−9.25
		$C_S = 1.01$	$C_S = 0.99$	$C_S = 0.99$
1.2×10^{-3}	1.59	−1.85	−1.95	−1.91
	4.31	−4.66	−4.76	−4.78
	7.22	−6.94	−7.22	−7.16
	8.19	−8.54	−8.55	−8.62
		$C_S = 0.97$	$C_S = 0.97$	$C_S = 0.98$
5.0×10^{-5}	1.54	−1.75	−1.88	−1.84
	4.38	−4.63	−4.90	−4.83
	6.79	−7.78	−9.71	−9.18
	9.39	−11.1	−10.9	−10.8
		$C_S = 1.20$	$C_S = 1.23$	$C_S = 1.21$

[a] Initiator concentration (mol dm^{-3}). [b] Ratio of dodecanethiol and monomer concentrations (10^{-3}). [c] Slope of ln($P(M)$) vs M in high molecular weight region (10^{-5}, see text). [d] Slope of ln($P(M)$) vs M in peak molecular weight region (10^{-5}, see text). [e] Slope of ln($P(M)$) vs M taken from peak to high molecular weight (10^{-5}, see text).

The Origin of the High Molecular Weight Limit in the CLD Procedure. We have already mentioned that the correct theoretical limit in the CLD procedure is at infinite molecular weights but also that the more reliable results seem to be obtained when using Λ(peak), i.e., the slope of a ln P plot in the region of the peak molecular weight of the GPC distribution. This finding is in agreement with the previous work of Moad and Moad.[19] Here, we will discuss this point in more detail, starting from a derivation of eq 2 which is analogous to the original derivation by Clay and Gilbert[14] but which is simpler and more general.

First, it needs to be realized that the instantaneous number distribution of *dead* polymer chains with chain length i, $P(i)$, contains contributions from termination by disproportionation and combination and from chain transfer (here we only include chain transfer to monomer and chain transfer agent):[14]

$$P(i) = P(i)_{comb} + P(i)_{disp} + P(i)_{tr,M} + P(i)_{tr,S} \qquad (3)$$

The individual contributions can be derived from the radical distribution by considering the corresponding reactions. For example, the contribution $P(i)_{\mathrm{tr,X}}$ from chain transfer to a species X (i.e., M or S) is given by

$$P(i)_{\mathrm{tr,X}} = k_{\mathrm{tr,X}}[\mathrm{X}][\mathrm{R}(i)] \tag{4}$$

where $[\mathrm{R}(i)]$ is the concentration of radicals with chain length i. Hence for transfer-dominated systems ($P(i)_{\mathrm{tr}} \gg P(i)_{\mathrm{comb}}, P(i)_{\mathrm{disp}}$), the shape of $P(i)$ is the same as the shape of the radical distribution. It turns out that this situation is in fact more general: Clay and Gilbert[14] have shown that $P(i)_{\mathrm{disp}}$ is often proportional to $[\mathrm{R}(i)]$, and $P(i)_{\mathrm{comb}}$ is sometimes so. These results are important because so long as $P(i)$ is proportional to $[\mathrm{R}(i)]$, then regardless of the mechanism of dead-chain formation (whether transfer-dominated or termination-dominated or a mixture of transfer and termination), the slope $\Lambda(i)$ of a plot of $\ln(P(i))$ vs i is equal to the slope $\Lambda_{\mathrm{R}}(i)$ of a plot of $\ln([\mathrm{R}(i)])$ vs i. In such circumstances one does not need to evaluate $P(i)$ in order to determine $\Lambda(i)$, because this quantity follows straight away from the radical distribution $[\mathrm{R}(i)]$. Hence we turn now to considering $[\mathrm{R}(i)]$.

To derive an expression for the radical distribution $[\mathrm{R}(i)]$, one needs to solve the population balance equations of the radicals:

$$\frac{\mathrm{d}[\mathrm{R}(i)]}{\mathrm{d}t} = \text{rate of appearance of } \mathrm{R}(i) - \text{rate of disappearance of } \mathrm{R}(i) \tag{5}$$

Radicals with a chain length of i ($i > 1$) are in general only created by the propagation of a radical with a chain length of $(i - 1)$, and they are lost by propagation, by chain transfer, and by termination with radicals of all chain lengths. Here we consider transfer to monomer and chain transfer agent only, but the generalization to include other forms of chain transfer is trivial (as will be clear). Transfer and propagation rates are chain length independent for chains longer than a few units,[29−32] so we assume here that only termination rate coefficients are chain-length dependent. Under these circumstances eq 5 becomes

$$\frac{\mathrm{d}[\mathrm{R}(i)]}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}(i-1)] - k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}(i)] - k_{\mathrm{tr,M}}[\mathrm{M}][\mathrm{R}(i)] - k_{\mathrm{tr,S}}[\mathrm{S}][\mathrm{R}(i)] - 2[\mathrm{R}(i)]\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j}[\mathrm{R}(j)] \tag{6}$$

The last term in this expression is the contribution from all termination events involving an i-meric radical, i.e., $2k_{\mathrm{t}}^{i,1}[\mathrm{R}(i)][\mathrm{R}(1)] + 2k_{\mathrm{t}}^{i,2}[\mathrm{R}(i)][\mathrm{R}(2)] + 2k_{\mathrm{t}}^{i,3}[\mathrm{R}(i)][\mathrm{R}(3)] + ...$ In the steady-state situation, in which the concentrations of radicals do not change, eq 6 can be rearranged to

$$\frac{[\mathrm{R}(i)]}{[\mathrm{R}(i-1)]} = \frac{k_{\mathrm{p}}[\mathrm{M}]}{k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + 2\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j}[\mathrm{R}(j)]} \tag{7}$$

From this equation, and using only the long-chain approximation, one can derive an expression for $\Lambda_{\mathrm{R}}(i)$, the slope of a plot of $\ln[\mathrm{R}(i)]$ vs i at any chain length i (see Appendix). This immediately becomes an expression for $\Lambda(i)$ if one has that $\Lambda_{\mathrm{R}}(i) = \Lambda(i)$, i.e., that $P(i) \propto [\mathrm{R}(i)]$. As already discussed, this is often the case, and in particular it is the case for dominant chain transfer, the situation in which we are most interested. So in what follows we assume that $\Lambda_{\mathrm{R}}(i) = \Lambda(i)$, in which case we have (see Appendix)

$$\Lambda(i) = \frac{\mathrm{d}\ln(P(i))}{\mathrm{d}i} = \frac{\mathrm{d}\ln[\mathrm{R}(i)]}{\mathrm{d}i} = -\left(C_{\mathrm{M}} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j}[\mathrm{R}(j)]}{k_{\mathrm{p}}[\mathrm{M}]}\right) \tag{8}$$

This equation reveals the potent and immediate connection between ln P plots and the values of kinetic parameters (as opposed to other more common ways of presenting molecular weight distributions). It is important to note about eq 8 that it does not depend on any assumptions concerning the termination mechanism. Also, one is reminded that the first part of eq 8—the equality $\Lambda(i) = \Lambda_{\mathrm{R}}(i)$—often holds under conditions where termination is a significant chain stopping event;[14] i.e., eq 8 is not just valid for conditions of transfer control.

The only term in eq 8 that depends on the chain length i is the termination term, and one can get a qualitative idea of how this term depends on the chain length through realizing that the termination reaction is diffusion-controlled.[33] As such, longer chains are expected to have a slower rate of termination. This means that the frequency of termination for a chain with length i, here denoted as $f_{\mathrm{t}}(i)$, and defined by eq 9, decreases with increasing i.

$$f_{\mathrm{t}}(i) = 2\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j}[\mathrm{R}(j)] \tag{9}$$

From eq 8 it is now easily seen that $-\Lambda(i)$ decreases with increasing i, and hence some curvature is introduced into a ln P plot. Whether or not this curvature is significant depends first on whether termination is making a significant contribution to $\Lambda(i)$ and second on whether $f_{\mathrm{t}}(i)$ is varying significantly with i. These are the issues which are now investigated.

For a more quantitative investigation of the chain-length dependence of $f_{\mathrm{t}}(i)$ it is necessary to know the form of $k_{\mathrm{t}}^{i,j}$. This has never been unambiguously determined from experiment, and besides, it is likely to vary with experimental conditions (e.g., it will depend on the polymer concentration of the system). Here we will be consistent with the original work of Clay and Gilbert,[14,34] and we will use the so-called diffusion mean expression for $k_{\mathrm{t}}^{i,j}$:

$$k_{\mathrm{t}}^{i,j} = \frac{1}{2}k_{\mathrm{t}}^{1,1}(i^{-a} + j^{-a}) \tag{10}$$

This expression is based upon the Smoluchowski equation, which is the generally applicable expression for the rate of a diffusion-controlled reaction;[35] i.e., one can be optimistic that the results which follow below from eq 10 are relevant for most real systems. In eq 10 $k_{\mathrm{t}}^{1,1}$ is the rate coefficient for termination between two monomeric radicals, and a is the scaling exponent for the dependence on chain length. For example, a would be approximately equal to 0.5 for a low-conversion system in which the rate-determining termination step was center-of-mass diffusion and the so-called reaction radius was independent of the i and j.[36] Importantly, the utilization of eq 10 does not impose any restriction on the value of a. For example, there is no reason eq 10 with $a = 0.16$ (i.e., the value applicable for segmental diffusion, see below) cannot be an accurate description of low conversion termination.

Using eq 10 and the expression for the average termination rate coefficient $\langle k_t \rangle$,[12] eq 11, the expression for the frequency of termination of an i-meric radical can be expressed more conveniently as in eq 12.

$$\langle k_t \rangle = \frac{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} k_t^{i,j}[\mathrm{R}(i)][\mathrm{R}(j)]}{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}[\mathrm{R}(i)][\mathrm{R}(j)]} = \frac{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} k_t^{i,j}[\mathrm{R}(i)][\mathrm{R}(j)]}{[\mathrm{R}^\bullet]^2} \tag{11}$$

$$f_t(i) = \langle k_t \rangle [\mathrm{R}^\bullet] + k_t^{1,1}[\mathrm{R}^\bullet] i^{-a} \tag{12}$$

After substitution of eq 12 into eq 8, an expression for $\Lambda(i)$ is obtained which only contains simple kinetic parameters:

$$\Lambda(i) = -\left(C_M + C_S \frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{\langle k_t \rangle [\mathrm{R}^\bullet]}{k_p[\mathrm{M}]} + \frac{k_t^{1,1}[\mathrm{R}^\bullet] i^{-a}}{k_p[\mathrm{M}]} \right) \tag{13}$$

It is clear that for chain-length-dependent termination (i.e., $a > 0$) the last term on the rhs of eq 13 approaches 0 for very large values of i, and hence taking the high molecular weight limit in eq 13 yields eq 14, which is identical to eq 2:

$$\lim_{i \to \infty} \Lambda(i) = \Lambda(\mathrm{high}) = -\left(C_M + C_S \frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{\langle k_t \rangle [\mathrm{R}^\bullet]}{k_p[\mathrm{M}]} \right) = \Lambda_{\mathrm{high}} m_0 \tag{14}$$

Therefore, based on *theoretical* grounds, the use of eq 2 is only valid in the *high* molecular weight limit. The question remains as to why, as clearly demonstrated here and in other studies, Λ(peak) yields the same and in many cases a more reliable result than Λ(high). An important practical reason for the reliability is the sensitivity of the high molecular weight region of the distribution to baseline selection, as extensively discussed by Moad and Moad.[19] In this paper our discussion will focus on understanding the behavior of $f_t(i)$, so that we can formulate guidelines for when $\Lambda(i)$ reaches its high molecular weight limit in practice.

We start by introducing a useful relationship, one which was originally derived by Mahabadi[10] and by Olaj and co-workers[11] and which links the average termination rate coefficient $\langle k_t \rangle$ to the average degree of polymerization $\mathrm{DP_n}$ of dead chains:

$$\langle k_t \rangle = A\,\mathrm{DP_n}^{-a} \tag{15}$$

Here a is the same exponent as in eq 10. Equation 15 has been extensively tested by Olaj and co-workers[37] and has been found to hold for several different mathematical formulations of $k_t^{i,j}$, including the diffusion mean given by eq 10. The precise value of the constant of proportionality A depends on such things as the value of a and how dead chains are formed[10,37] (e.g., dead chain formation by combination obviously gives a larger DP_n and hence a larger A). Nevertheless, one can say that $A \approx k_t^{1,1}$, in which event eq 12 can be rewritten as

$$f_t(i) \approx k_t^{1,1}[\mathrm{R}^\bullet](\mathrm{DP_n}^{-a} + i^{-a}) \tag{16}$$

Alternatively, one may write

$$\frac{f_t(i{=}x\mathrm{DP_n})}{\langle k_t \rangle [\mathrm{R}^\bullet]} = 1 + x^{-a} \tag{17}$$

The reason for expressing $f_t(i)$ in the form of eq 17 will become clear below. Before proceeding we note that because A is not exactly equal to $k_t^{1,1}$, eqs 16 and 17 are not exact. However, they should be acceptably accurate, and so they are used for further discussion.

One sees from eqs 16 and 17 that for a chain length i which is equal to the average degree of polymerization $\mathrm{DP_n}$ (i.e., $i = \mathrm{DP_n}$, $x = 1$), $f_t(i)$ is equal to $2\langle k_t \rangle[\mathrm{R}^\bullet]$. This is of interest because it is the value of $f_t(i)$ for all i in the so-called classical limit, in which one has chain-length-independent termination. To see this, either substitute $k_t^{i,j} = \langle k_t \rangle$ into eq 9 or $a = 0$ into eq 17. Assuming now that termination is chain length dependent, i.e., $a > 0$, then for $i < \mathrm{DP_n}$ ($x < 1$), eqs 16 and 17 give $f_t(i) > 2\langle k_t \rangle[\mathrm{R}^\bullet]$. This means that the radicals terminate faster than in the classical limit. On the other hand, for $i > \mathrm{DP_n}$ ($x > 1$) it is evident that the radicals terminate more slowly than in the classical limit. Further, according to eqs 16 and 17 the limiting value of $f_t(i)$ is $\langle k_t \rangle[\mathrm{R}^\bullet]$. Thus, eq 17 can be seen as expressing the relative magnitude of $f_t(i)$ compared to the high molecular weight limit of this quantity.

For practical purposes the region of a ln P plot in which one is interested is that for which $i \geq \mathrm{DP_n}$. From the above discussion it is clear that for such radical chain lengths the frequency of termination lies between $2\langle k_t \rangle[\mathrm{R}^\bullet]$ and $\langle k_t \rangle[\mathrm{R}^\bullet]$. This is a general result, independent of the dominant reaction(s) by which dead chains are actually formed. Its relevance in terms of the slopes of ln P plots is now explained. The dead chain formation by chain transfer in the absence and in the presence of a significant contribution by termination is distinguished and discussed in turn.

Dead Chain Formation by Chain Transfer with a Negligible Termination Contribution. This requires that the frequency of dead polymer formation by chain transfer is much larger than the frequency of termination, i.e., $k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] \gg 2\langle k_t \rangle[\mathrm{R}^\bullet]$. So it follows from above that any possible curvature in a ln P plot will be negligible for $i > \mathrm{DP_n}$, because termination is making a negligible contribution to $\Lambda(i)$, and the dominant chain transfer contributions are chain length independent. This is the case which Moad and Moad[19] previously discussed in great detail and which is clearly demonstrated with the present experimental results. The recommendation of Moad and Moad is therefore endorsed: the $\Lambda(i)$ which should be used for chain transfer constant evaluation is Λ(peak).[19]

Dead Chain Formation by Chain Transfer with a Significant Termination Contribution. In this case $k_{\mathrm{tr,M}}$-

Table 5. Dependence of Frequency of Termination of Radicals with Characterictic Chain Lengths on the Scaling Exponent

	$f_t(i{=}x\mathrm{DP}_n)/\langle k_t\rangle[\mathrm{R}^\bullet]$				
x	$a = 0$	$a = 0.16$	$a = 0.5$	$a = 1$	$a = 2$
1	2.00	2.00	2.00	2.00	2.00
2	2.00	1.90	1.71	1.50	1.25
6	2.00	1.75	1.41	1.17	1.03
10	2.00	1.69	1.32	1.10	1.01

$[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] \approx 2\langle k_t\rangle[\mathrm{R}^\bullet]$, and termination is obviously contributing to $\Lambda(i)$. This is of less interest in terms of determining chain transfer constant values, because significant curvature in the ln P plot can be introduced as will be clear from the discussion below. However, it is of interest in terms of the possibility of using eq 2 to obtain values of the average termination rate coefficient, $\langle k_t\rangle$. Specifically, there is the suggestion that if $\Lambda(\text{high})$ could be obtained experimentally, then $\langle k_t\rangle = -\Lambda(\text{high})k_p[\mathrm{M}]/[\mathrm{R}^\bullet]$ follows (see eq 2). The important issue to consider here is whether $\Lambda(\text{high})$ can be obtained experimentally when one has significant termination, i.e., whether $\Lambda(i)$ converges to its limiting value, $\Lambda(\text{high})$, at chain lengths such that one has a significant GPC signal. To investigate this, we note that $\Lambda(i) = -f_t(i)/(k_p[\mathrm{M}])$ in the limiting case of dominant termination (see eqs 8 and 9) and that the value at infinite chain lengths of $f_t(i)$ is $\langle k_t\rangle[\mathrm{R}^\bullet]$. It now follows from eq 17 that

$$\left(\frac{\Lambda(i)}{\Lambda(\text{high})}\right)_{\text{dominant termination}} = \frac{f_t(i{=}x\mathrm{DP}_n)}{\langle k_t\rangle[\mathrm{R}^\bullet]} = 1 + x^{-a} \tag{18}$$

(Actually, with termination control one only has $P(i) \propto [\mathrm{R}(i)]$ when $f_t(i)$ is independent of i, so strictly speaking eq 18 is not a valid expression for $\Lambda(i)/\Lambda(\text{high})$. However, accounting for this only serves to introduce more curvature into a ln P plot, so in fact the arguments below are strengthened rather than undermined.)

In Table 5 we have used eq 18 to list values of $f_t(i{=}x\mathrm{DP}_n)/(\langle k_t\rangle[\mathrm{R}^\bullet])$ for several characteristic chain lengths, viz., $x = 1$ $(=M_n)$, $x = 2$ $(\approx M_w)$, $x = 6$ (approximately equal to M_{z+1} for practical purposes), and $x = 10$ (typically where the end of a SEC distribution occurs). We have also used a range of different termination scaling exponents, viz., $a = 0$ (classical), $a = 0.16$ (segmental diffusion control of the termination rate), $a = 0.5$ (appropriate for center-of-mass diffusion at low conversion), $a = 1$ (center-of-mass diffusion at medium conversion), and $a = 2$ (diffusion by reptation).[12,36,38] It can be seen from Table 5 that, as already discussed, $f_t(i)$ in the region of M_n is equal to $2\langle k_t\rangle[\mathrm{R}^\bullet]$ for all values of a. This means that in the region of M_n the slope $\Lambda(i)$ of a ln P plot is twice its limiting value (see eq 2). Thus, it is inappropriate to take $\Lambda(i)$ from this region of a ln P plot and assume it is equal to $\Lambda(\text{high})$. The situation at higher-i regions of a ln P plot depends on the value of a. For the larger values of a, especially $a = 2$, $\Lambda(i)$ rapidly drops to $\Lambda(\text{high})$; e.g., for $a = 2$ one has that $\Lambda(i)$ is about $1.3\Lambda(\text{high})$ in the region around M_w. Under such circumstances it is reasonable to take $\Lambda(i)$ at the peak molecular weight and use this value as $\Lambda(\text{high})$ in eq 2. However, for lower values of a the value of $\Lambda(i)$ in the region around M_w is much closer to $2\Lambda(\text{high})$ than to $\Lambda(\text{high})$; in fact, for $a = 0.16$ (and obviously also for $a = 0$) this is true for the entire distribution. Hence, for lower values of a the use of eq 2 for the study of termination rate coefficients is problematic, because it is evident that the accurate measurement of $\Lambda(\text{high})$ is unlikely to be possible. This is especially so at low conversions, where 0.5 is an upper bound for a,[36] and in fact the value of a is likely to be much less than this, probably being around 0.16.[39−41] One also should not forget that for $a = 0$ (chain-length independence) eq 2 does not hold as written. In general, the value of a is an unknown quantity, so it is clear that if it is used at all for the detailed study of termination rate coefficients, then eq 2 should only be used cautiously, because what one assumes is an experimental value of $\Lambda(\text{high})$ may in fact be in error by a factor of 2 (admittedly not a large error as measurement of $\langle k_t\rangle$ goes). An experimental study[42] in which values of $\Lambda(i)$ were used to determine values of $\langle k_t\rangle$ via eq 2 should be evaluated in this light. In view of the above findings it would seem sensible to recommend the use of the full equation for $\Lambda(i)$, eq 8, rather than its limiting form, eq 2, for the modeling of ln P plots when termination is the dominant, or indeed even a significant, chain-stopping event.

Last, we point out that strictly speaking the above conclusions are tied to the model that has been used for $k_t^{i,j}$, viz. eq 10. In work being prepared for publication we have shown that the use of a different functional form for $k_t^{i,j}$ will lead to a different expression for $\Lambda(i)$, sometimes the limiting expression for $\Lambda(i)$ even being different from eq 2 (e.g., the case of the so-called geometric mean).[37] This further serves to emphasize that eq 2 should only be used with caution for studying termination.

Use of Mayo and CLD Methods for the Measurement of Chain Transfer Constants to Monomer. So far our discussion has focused mostly on the measurement of chain transfer constants to chain transfer agents and has touched briefly on the determination of $\langle k_t\rangle$. In the former case it was shown that both Mayo and CLD procedures are robust and, more importantly, generate the same results. In this section we will briefly discuss the use of both methods for the measurement of chain transfer constants to monomer, C_M, and it will become clear that the CLD procedure provides the simpler, and probably more reliable, means to this end.

First, we will discuss the Mayo procedure as it is followed *conventionally*. Experiments are carried out in the absence of chain transfer agent, so that the only chain transfer events are to monomer (since this is the rate parameter which is to be determined). Replacing the overall radical concentration by $R_p/(k_p[\mathrm{M}])$, where R_p is the rate of polymerization, eq 1 then becomes[7]

$$\frac{1}{\mathrm{DP}_n} = (1+\lambda)\frac{\langle k_t\rangle R_p}{k_p^{\,2}[\mathrm{M}]^2} + C_M \tag{19}$$

From eq 19 it is easily seen that if one measures DP_n and R_p and plots these data as DP_n^{-1} vs R_p,[11,43] then C_M can be obtained as the intercept of this plot. This result is not invalidated by termination being chain length dependent. However, the common procedure is to obtain C_M as the *straight-line* intercept of a plot of DP_n^{-1} vs R_p, and it is evident that this is only correct if *all* other parameters in the first term of the rhs remain *constant* as R_p varies. This condition is not met if termination is chain length dependent, because changes in DP_n directly result in changes in $\langle k_t\rangle$ (see eq 15). Whether or not this effect is significant in practice is not a priori known, as it depends on the severity of the chain-length dependence of termination, i.e., on the value of a.[11] For example, for $a = 0.16$ (likely low conversion value[39,40]) the curvature of Mayo plots is minimal, and negligible error is introduced by linear fitting of such plots.[11] However, in at least one set of experimental studies,[22] cases of significant nonlinearity seem to have been observed. The way around this problem is of course just to carry out nonlinear fitting of a plot of $\mathrm{DP_n}^{-1}$ vs R_p. Even so, to determine C_M one is still left with the uncertainty of having to extrapolate what may be a significantly nonlinear plot to $R_p = 0$.

In contrast, the measurement of C_M using the CLD procedure would appear to be a simpler procedure. In the absence of chain transfer agent, eq 8 becomes

$$\Lambda(i) = -\left(C_M + \frac{2\sum_{j=1}^{\infty} k_t^{i,j}[\mathrm{R}(j)]}{k_p[\mathrm{M}]}\right) \tag{20}$$

For the diffusion mean model of termination (eq 10), one obtains from eq 20 the following limiting result (see eq 2):

$$\Lambda(\mathrm{high}) = -\left(C_M + \frac{\langle k_t\rangle[\mathrm{R}^\bullet]}{k_p[\mathrm{M}]}\right) \tag{21}$$

Whichever of the above equations one considers, it is immediately clear that, in the absence of chain transfer agent, the slope of a ln P plot is equal to $-C_M$ when the contribution of termination is negligible. This latter condition is to be noted, because there may exist the impression that $-C_M$ can be obtained as the limiting slope of *any* ln P plot. In fact this is not so, as eq 21 clearly reveals. Rather, $\Lambda(\mathrm{high}) = -C_M$ only when $C_M \gg (\langle k_t\rangle[\mathrm{R}^\bullet])/(k_p[\mathrm{M}])$; i.e., when the frequency of termination of long chains is negligible compared to the frequency with which they undergo chain transfer to monomer. Such a situation can be realized by reducing the initiator concentration (and hence the overall radical concentration) until $\Lambda(\mathrm{high})$ remains constant upon further reduction of initiator concentration. Under such conditions $\Lambda(i)$ will be independent of i certainly for $i > \mathrm{DP_n}$, because if $k_{\mathrm{tr,M}}[\mathrm{M}] \gg \langle k_t\rangle[\mathrm{R}^\bullet]$, then one also has that $k_{\mathrm{tr,M}}[\mathrm{M}] \gg 2\langle k_t\rangle[\mathrm{R}^\bullet]$. So a *necessary* and *sufficient* condition for determination of C_M is an extremely low rate of initiation. But as long as one is in this limit of dominant chain transfer to monomer, $\Lambda(i)$ for any $i > \mathrm{DP_n}$ will be as good as equal to $\Lambda(\mathrm{high})$. So exactly as with determination of C_S, it is recommended that C_M should be determined from $\Lambda(\mathrm{peak})$ rather than $\Lambda(\mathrm{high})$, because one does not need to go to this limit.

From the above discussion, one could easily conclude that the CLD procedure for measurement of C_M is preferable to the Mayo procedure from an experimental viewpoint. This is because both procedures in principle require the same thing, namely reduction of initiator concentration until $[\mathrm{R}^\bullet]$ and therefore R_p approaches zero, and yet the Mayo procedure also requires the accurate measurement of very low rates of polymerization (which can be difficult), whereas the CLD procedure only requires the determination of the molecular weight distribution. However, this conclusion would be premature. If one compares eq 1 with eq 21, it is clear that for both procedures the measured quantity (i.e., $\mathrm{DP_n}^{-1}$ or $-\Lambda(\mathrm{high})$) becomes equal to C_M as $\langle k_t\rangle[\mathrm{R}^\bullet]/(k_p[\mathrm{M}])$ becomes negligible in comparison to C_M. In other words, *both the Mayo and CLD procedures require exactly the same conditions*, namely extrapolation to $[\mathrm{I}] = 0$ (or conditions such that [I] is effectively zero). This implies that if it is sufficient to reduce the initiator concentration until $-\Lambda(\mathrm{high})$ is constant and a minimum, it should also be sufficient to reduce the initiator concentration until M_n and M_w are constant and at maximum values. In fact, Stickler and Meyerhoff took advantage of exactly this result in their determination of C_M for methyl methacrylate.[23] Hence, knowledge of the rate of polymerization is also *not* essential for the use of the Mayo procedure.

To our knowledge, not many studies have explicitly compared the performance of the Mayo and CLD procedures for the measurement of C_M, so our observation above still requires experimental verification. However, we are aware of one recent study that explicitly compares the two procedures,[22] and it suggests the possible correctness of our observation. In this study, C_M values were determined for methyl methacrylate, styrene, and α-methylstyrene. So it seems that also for the determination of chain transfer constants to monomer the Mayo and CLD procedures are completely equivalent, although this should be further tested with more careful experiments.

Overall Comparison of Mayo and CLD Methods. In this paper we have seen that both Mayo and CLD procedures can be used to determine values of chain transfer constants to chain transfer agent, C_S, of chain transfer constants to monomer, C_M, and, in principle, of average termination rate coefficients, $\langle k_t\rangle$. In each case we now discuss which method might be preferable to use in practice.

Chain Transfer Constants to Chain Transfer Agent. The present study clearly shows that the Mayo and CLD procedures are equally suitable for the determination of C_S values, yielding the same results within experimental error. Both procedures require the same amount of experimental work, the difference lying in the analysis of the size-exclusion chromatograms. Whereas most standard SEC software packages directly provide the user with the common molecular weight averages and distributions (e.g., $w(\log M)$ and $w(M)$), the ln P plots need to be separately constructed from the provided data. This procedure can be quite time-consuming when a large number of molecular weight distributions need to be analyzed. However, this drawback could be easily remedied if the demand for this particular information were high enough for the suppliers of commercial SEC software to include this option automatically.

Another drawback of the CLD procedure is that, in our experience, ln P plots often show significant curvature, even in circumstances in which they should be completely straight, and one can be confident that negligible error has been introduced from analysis (e.g., baseline selection) of the size-exclusion chromatogram. This curvature can easily be introduced by less than perfect columns used in the SEC setup (e.g., columns leading to significant SEC broadening) and is therefore a serious problem in this procedure. In such cases it is difficult to select a straight region in a ln P plot, and some undesired subjectivity is introduced into the CLD procedure. It is therefore more desirable to use $M_w/2$, which is unique for the distribution (as opposed to a varying $\Lambda(i)$). Experience in our laboratory has indicated that, in cases in which significant curvature occurs, the results based upon the Mayo procedure using $M_w/2$ agree very well with the results obtained from the CLD procedure using Λ_{peak} (vide supra).[5,26,27] Hence, in accordance with the recommendation made by Moad and Moad,[19] we conclude that the use of Λ_{peak} probably leads to more reliable results than the use of Λ_{high}.

This inconvenience of the CLD procedure is more than compensated for in a number of ways. As mentioned early on in this paper, M_n is the average molecular weight yielded least accurately by SEC, for well-known reasons. This is a difficulty of the Mayo method and is why it is recommended to use $M_w/2$ instead (although note that this can only be done with confidence for transfer-dominated systems). In particular, the Mayo method encounters problems with low molecular weight polymer.[6] In such cases the determination of M_n is often extremely difficult, and even if M_w can be determined accurately, the exact value of the polydispersity index may not be known (it will be less than 2 for very low molecular weight systems), in which case M_n cannot be accurately estimated from M_w. By contrast, the CLD procedure requires only an accurate value of $\Lambda(i)$, which will be available from the higher molecular weight region of the distribution. Another situation when the CLD procedure is more useful is when one must analyze a contaminated polymer sample. A contamination (of an arbitrary nature) may alter the molecular weight distribution and will therefore significantly change the molecular weight averages, rendering the Mayo procedure useless. However, if a region in the molecular weight distribution can be identified in which the distribution is less affected by the contaminant, this region can still be used in the CLD procedure.[19,24,44] The CLD procedure is also expected to be more robust when one has systematic error in SEC calibration, because then the obtained molecular weight averages will not be accurate, but the systematic error in values of $P(M)$ can be expected to cancel out to some extent when the slope of a ln P plot is taken.

Before proceeding, we point out that some of the aforementioned considerations obviously apply in general, not just when one is determining C_S.

Chain Transfer Constants to Monomer. As discussed in the previous section, the choice between the two procedures in the determination of the chain transfer constant to monomer seems to be a simple one. Whereas the CLD procedure involves the measurement of Λ for decreasing initiator concentrations until Λ is constant, the conventional Mayo procedure involves the measurement of both DP_n *and* the rate of polymerization for decreasing initiator concentrations. Besides the fact that the Mayo procedure involves more work, it also intrinsically suffers from the fact that the plot involved may not be straight, and hence extrapolation to find the intercept may be difficult. However, as we discussed in the previous section, it is most likely that the Mayo procedure can be carried out in exactly the same way as the CLD procedure, i.e., through reduction of the initiator concentration until M_w is constant. We stress that this suggestion still needs to undergo rigorous experimental verification.

Average Termination Rate Coefficients. We have seen that in principle $\langle k_t\rangle$ may be determined from Λ_{high}. Similarly, referring to eq 19 it is evident that $(1 + \lambda)\langle k_t\rangle$ may be obtained from the straight-line slope of a Mayo plot of $\mathrm{DP_n}^{-1}$ vs R_p.[7] To obtain $\langle k_t\rangle$, one then needs to know the value of λ, the fraction of termination by disproportionation. This is usually not known with any confidence, and so in principle it is a small advantage of the CLD procedure that $\langle k_t\rangle$ may be determined without needing to know the value of λ. That said, it has been seen that the use of the CLD procedure for determining $\langle k_t\rangle$ is in general problematic, because $\Lambda(i)$ values often converge to Λ(high) only at chain lengths such that $\Lambda(i)$ cannot be determined accurately. This is because at very high molecular weights a GPC signal is so small that $\Lambda(i)$ is totally hostage to baseline selection, as shown by Moad and Moad.[19] Also, Λ_{high} values are distorted by SEC broadening. In fact, these are the reasons why it is such a significant result that $\Lambda(\text{high}) = \Lambda(\text{peak})$ for transfer-dominated systems: Λ_{peak} is not very sensitive to baseline selection[19] or to SEC broadening, and so it should always be used with the CLD procedure where it is theoretically justified to do so.

The above discussion is not to imply that the Mayo procedure is preferable for determination of $\langle k_t\rangle$. This is because the Mayo procedure for determining $\langle k_t\rangle$ is clearly only meaningful when termination is chain length independent, and thus $\langle k_t\rangle$ is constant as R_p varies[43] (in which event the CLD procedure with a modified eq 2 becomes robust, because then $f_t(i)$ is equal to $2\langle k_t\rangle[\mathrm{R}^\bullet]$ and so is independent of i). But in the expected event of termination being chain length dependent, it is not clear whether a Mayo plot offers any prospects for information about values of $\langle k_t\rangle$ and how they vary. On the other hand, an elegant feature of the CLD procedure is the way it provides an opportunity for determining $\langle k_t\rangle$ from a fundamental feature of a molecular weight distribution (viz., Λ_{high}) when termination is chain length dependent. It is just that in practice the prospects for accurate determination of Λ_{high} may not be good, and also the theoretical expression for Λ_{high} depends on the (unknown) functional form of $k_t^{i,j}$ (see above).

On the basis of the preceding discussion, neither of the simple molecular weight-based methods for determining $\langle k_t\rangle$ can be strongly recommended, although the CLD procedure is obviously preferable in view of it being more general. This is the topic of ongoing investigations. At this stage it would seem most wise to recommend modeling of molecular weight distributions as a whole if one wants to obtain information about termination rate coefficients.

Conclusions

In this paper we have shown that the Mayo and chain length distribution procedures for determining kinetic constants are in essence the same. To some extent this is evident just by comparing eqs 1 and 2. For example, when chain transfer is dominant, it is immediately clear that $\mathrm{DP_n}^{-1} = -\Lambda(\text{high})$, and so both procedures are equivalent in theory for the measurement of chain transfer constants. But what about in practice? This too has been a major topic of this paper. We have shown that both procedures yield reliable results for the study of chain transfer agents, with the most reliable values of C_S being obtained by using $M_w/2$ in the Mayo procedure and Λ(peak) in the CLD procedure. Although the use of the Mayo procedure is much simpler in the case of an ordinary experiment with “nice” distributions, the CLD procedure has more advantages when dealing with very low molecular weights or with contaminated polymer samples. With regard to determination of chain transfer constants to monomer, although in theory the CLD and Mayo procedures are still completely equivalent, more experimental investigations are required to confirm this in practice.

Whatever the similarities of the Mayo and CLD procedures, it would seem appropriate to recommend that where possible cross checks should be perfomed to establish the consistency of the obtained results. Also recommended are ln *P* plots as a meaningful way of looking at molecular weight distribution data. This is because there is an intimate and immediate connection between kinetic parameters and the derivative of a ln *P* plot, as eq 8 makes clear.

Last, readers are reminded that eqs 1 and 2 are both underpinned by the long chain and steady-state approximations. Because of the assumption of steady-state conditions, the Mayo and CLD procedures should only be used for analyzing results from continuously initiated polymerizations carried out over a small conversion range. That said, there is evidence that steady-state relations sometimes apply under conditions of periodic initiation,[17,39,40] so there is the possibility that eqs 1 and 2 may be more widely applicable. However, this should never be an a priori assumption.

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Appendix

The steady-state expression for the radical distribution is given by (eq 7)

$$\frac{[\mathrm{R}(i)]}{[\mathrm{R}(i-1)]} = \frac{k_\mathrm{p}[\mathrm{M}]}{k_\mathrm{p}[\mathrm{M}] + k_{\mathrm{tr,M}}[\mathrm{M}] + k_{\mathrm{tr,S}}[\mathrm{S}] + 2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[\mathrm{R}(j)]} \tag{A1}$$

$$\Rightarrow \frac{[\mathrm{R}(i)]}{[\mathrm{R}(i-1)]} = \left(1 + C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[\mathrm{R}(j)]}{k_\mathrm{p}[\mathrm{M}]}\right)^{-1} \tag{A2}$$

Because polymerization forms long chains, the probability of a radical undergoing chain transfer or chain termination is very small. Hence, the frequency ratios on the rhs of eq A2 are very small compared to 1:

$$C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[\mathrm{R}(j)]}{k_\mathrm{p}[\mathrm{M}]} \ll 1 \tag{A3}$$

In the so-called long-chain limit, all the frequency ratios are so close to zero that eq A2 can be rewritten as

$$\Rightarrow \frac{[\mathrm{R}(i)]}{[\mathrm{R}(i-1)]} = \exp\left\{-\left(C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[\mathrm{R}(j)]}{k_\mathrm{p}[\mathrm{M}]}\right)\right\} \tag{A4}$$

$$\Rightarrow \ln[\mathrm{R}(i)] - \ln[\mathrm{R}(i-1)] = -\left(C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[\mathrm{R}(j)]}{k_\mathrm{p}[\mathrm{M}]}\right) \tag{A5}$$

The lhs of eq A5 can then be written as a difference quotient:

$$\ln[\mathrm{R}(i)] - \ln[\mathrm{R}(i-1)] = \frac{\ln[\mathrm{R}(i)] - \ln[\mathrm{R}(i-1)]}{1} = \frac{\Delta \ln[\mathrm{R}(i)]}{\Delta i} \tag{A6}$$

Because a radical distribution is actually discrete rather than continuous, eq A6 is in fact an exact expression for the derivative of ln[R(*i*)] with respect to *i*, i.e.,

$$\Lambda_\mathrm{R}(i) = \frac{\mathrm{d}\ln[\mathrm{R}(i)]}{\mathrm{d}i} = \lim_{\Delta i \to 1} \frac{\Delta \ln[\mathrm{R}(i)]}{\Delta i} \tag{A7}$$

Hence eq A5 becomes

$$\Lambda_\mathrm{R}(i) = -\left(C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + \frac{2\sum_{j=1}^{\infty} k_\mathrm{t}^{i,j}[\mathrm{R}(j)]}{k_\mathrm{p}[\mathrm{M}]}\right) \tag{A8}$$

As a description of the radical distribution [R(*i*)], the above equation holds for all *i*, and it holds regardless of which kinetic events are dominant. Our derivation of eq A8 is in essence the same as that of Clay and Gilbert,[14] except that we have (more correctly) used equations for a discrete rather than a continuous radical distribution, and we have not restricted ourselves to a particular termination model. Also, by generalizing the derivation it has become simpler.

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