Homopolymerizations of Methyl Methacrylate and Styrene: Chain Transfer Constants from the Mayo Equation and Number Distributions for Catalytic Chain Transfer, and the Chain Length Dependence of the Average Termination Rate Coefficient

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ABSTRACT: The catalytic chain transfer agent [bis[μ-[(2,3-butanedione dioximato)(2−)-*O,O′*]] tetrafluorodiborato(2−)-*N,N′,N″,N‴*]cobalt (COBF) was investigated in polymerizations of methyl methacrylate and styrene in bulk and in methyl methacrylate in toluene solution. A wide range of polymer molecular weights were produced by these reactions under identical polymerization conditions, enabling the use of these reactions in the examination of the chain length dependence of the average termination rate coefficient. A strong chain length dependence in accord with theoretical predictions for diffusion-controlled termination was observed. A total of five variations of the use of the Mayo equation and the shape of the number distribution were compared as methods of evaluating the chain transfer activity of COBF. MALDI-TOF mass spectrometry and SEC were evaluated for measuring the number distributions of the polymers and deficiencies were exhibited in the distributions from MALDI-TOF. Both the number distribution and Mayo treatments of the data gave similar results. COBF was shown to have a very high chain transfer activity in all of these polymerizations. Chain transfer activities of ca. 36 000 were found for COBF in bulk MMA, ca. 25 000 for MMA in toluene solution, and ca. 1500 for bulk styrene. A marked solvent effect is shown for toluene in the COBF-mediated polymerization of MMA.

Introduction

The utility of a polymer in an application depends on its physical properties. The molecular weight distribution of a polymer can strongly influence many of these properties (i.e. melt processability, solution viscosity, glass transition temperature, and gel content). As a result molecular weight control is an important area in the field of addition polymerization. Addition of a chain transfer agent is the most direct method of altering the molecular weight distribution in free-radical polymerization. In commercial free-radical polymerizations, these chain transfer agents are generally mercaptans. Catalytic chain transfer has arisen as the most effective method for molecular weight reduction in free-radical polymerizations containing methacrylates.

Catalytic chain transfer polymerization (CCTP) has been the subject of some recent reviews.[1,2] It occurs when certain low-spin cobalt(II) macrocycles are added to free-radical polymerizations (generally containing methacrylates). The mode of action of these catalytic chain transfer agents (CCTAs) is as yet unclear and discussed in these reviews. CCTAs differ significantly from conventional chain transfer agents in that they are not consumed during the transfer reaction. CCTAs are the most effective chain transfer agents known, and are compatible with a wide variety of functional monomers such as hydroxyl, amino, carboxylic acid, etc. and are active under heterogeneous polymerization conditions (e.g. emulsion).[3,4]

The effectiveness of a chain transfer agent is measured by the chain transfer constant, C_S, defined as the ratio of the rate constant for the chain transfer reaction to the rate constant for propagation:

$$C_S = k_{tr,s}/k_p \tag{1}$$

C_S values for very effective conventional chain transfer agents (e.g. mercaptans) are on the order of 1 for methacrylates.[5] In contrast, the chain transfer constants for CCTAs are 4 orders of magnitude greater, of the order of 30 000 for methacrylates.[6]

Traditionally chain transfer constants have been determined using variations of the Mayo equation,[7,8] a form of it being given below:

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_S\frac{[S]}{[M]} \tag{2}$$

DP_n is the number-average degree of polymerization of the polymer, DP_{n0} is the number-average degree of polymerization for polymer produced under the same conditions in the absence of added chain transfer agent, and [S] and [M] are the concentrations of added chain transfer agent and monomer, respectively. The use of eq 2 to produce a Mayo plot is the most generally accepted method for determining chain transfer constants and has been used to determine the bulk of chain transfer constants to date.

The basis of the Mayo plot is that chain transfer is a chain-breaking event which will affect the number-average degree of polymerization. The Mayo plot relies on the number and nature (i.e. combination and disproportionation) of kinetic chain initiation and termination (as opposed to transfer) events remaining constant both in the presence and in the absence of chain transfer agent. More succinctly, DP_{n0} must remain constant. In the presence of a chain transfer agent, more polymer chains are produced relative to polymerization in the absence of CTA. This increase is quantified in the left-hand term of eq 2 and is related to the relative levels of chain transfer agent through the right-hand term.

Equation 2 can be expanded in to a form which expresses it in terms of the fundamental rate coefficients in a free-radical polymerization. This is given in eq 3.

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F_c represents the fraction of termination by combination, R_p represents the rate of polymerization, k_p is the propagation rate constant, R_I is the rate of initiation, and M, I, and Sol, refer to monomer, initiator, and solvent, respectively.

$$\frac{1}{\mathrm{DP_n}} - \left(\frac{(2 - F_c)R_I}{2R_p k_p^2[\mathrm{M}]^2} + C_M + C_I\frac{[\mathrm{I}]}{[\mathrm{M}]} + C_{sol}\frac{[\mathrm{Sol}]}{[\mathrm{M}]}\right) = C_S\frac{[\mathrm{S}]}{[\mathrm{M}]} \quad (3)$$

Recently, an alternative to the Mayo plot has emerged[9-13] from theoretical considerations of polymerization kinetics. Unlike the Mayo plot, this method does not rely on molecular weight averages; instead it uses the shape of the number distribution (which is trivially related to the molecular weight distribution) of the polymer. The number distribution of a polymer, $N(M)$, is obtained by expressing the number of polymer molecules of a given molecular weight as a function of molecular weight. In this work number distributions from matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and size exclusion chromatography (SEC) are of interest. In principle the number distribution is obtained directly from the MALDI-TOF experiment. The relationship of the number distribution to the molecular weight distribution and SEC chromatogram is more complicated and has been discussed in detail elsewhere.[14] It will simply be stated that the number distribution can be obtained by dividing the signal from the SEC (assuming that the detector signal is proportional to the weight of polymer eluting through the detector) by the product of the slope of the calibration curve and the molecular weight of the polymer eluting at that elution volume.

The number distribution can also be expressed in terms of degree of polymerization as opposed to molecular weight, and this form of the number distribution will be used throughout this work. The two number distributions are trivially related by $N(\mathrm{DP}) = N(M/M_0)$, where M_0 is the molecular mass of the repeat unit.

The number distribution of a polymer contains a history of the kinetic events which occurred to produce that polymer, and it has been demonstrated that information on chain transfer kinetics can be readily extracted from the number distribution of a polymer. This method is based on the realization under the conditions used in many radical polymerizations the number distributions of the resultant polymers are dominated by a simple exponential decay. In a system where the two dominant modes of termination are by termination between a long and a short chain and by chain transfer, at low conversions theory suggests the number distribution is expected to have the following form at high degrees of polymerization:[9]

$$N(\mathrm{DP}) = \exp\left(-\frac{k_{tr,M}[\mathrm{M}] + \langle k_t\rangle[\mathrm{R}^\bullet] + k_{tr,S}[\mathrm{S}] + \sum k_{tr,C}[\mathrm{C}]}{k_p[\mathrm{M}]}\mathrm{DP}\right) \quad (4)$$

where $\langle k_t\rangle$ is the average termination rate coefficient, $[\mathrm{R}^\bullet]$ is the radical concentration, and $\sum k_{tr,C}[\mathrm{C}]$ accounts for chain transfer to the other components in the system except for polymer (initiator, solvent, etc.). Chain transfer to polymer is assumed to be negligible. A plot of the negative slope of the natural logarithm of the number distribution versus [S]/[M] for several different values of [S]/[M] has slope equal to C_S and intercept equal to the contribution from the other terms.[13] This method is the conventional means of using the number distribution to obtain chain transfer constants for added chain transfer agents.

As the most effective method of controlling molecular weight, CCTP is also useful in studying phenomena such as the chain length dependence of the termination rate coefficient. It allows polymers with a wide variety of molecular weights to be obtained under essentially the same polymerization conditions; only ppm levels of the CCTA are required to give large molecular weight reductions. The chain length dependence of termination reactions is one of the most poorly understood areas in free-radical polymerization kinetics.[5,15] A major reason for this is that, from a practical perspective, it is a very difficult phenomenon to study.

The average termination rate coefficient is expected to show a chain length dependence. This dependence will manifest itself in the rate data of CCTP reactions performed under the same conditions but producing a wide range of molecular weights. The average termination rate coefficient can be formally defined as in eq 5.[9]

$$\langle k_t\rangle = \frac{\sum_i\sum_j k_t^{ij}[\mathrm{R}^\bullet]_i[\mathrm{R}^\bullet]_j}{(\sum_i[\mathrm{R}^\bullet]_i)^2} \quad (5)$$

where the subscripts i and j refer to the chain length of the radical and k_t^{ij} refers the rate constant for termination between radicals of length i and j, respectively. Hereafter, the average termination rate coefficient defined in eq 5 will be referred to as the termination rate coefficient. Using this definition, the rate of termination, R_t, can be expressed as eq 6. Following the convention for initiation with a thermal free-radical initiator, the rate of initiation is defined in eq 7 and the propagation rate in eq 8.

$$R_t = 2\langle k_t\rangle[\mathrm{R}^\bullet]^2 \quad (6)$$

$$\mathrm{R_I} = 2fk_d[\mathrm{I}] \quad (7)$$

$$R_p = k_p[\mathrm{R}^\bullet][\mathrm{M}] \quad (8)$$

For a series of identical polymerizations, except for the amount of catalytic chain transfer agent that they contained, the rate of initiation, the propagation rate constant, and the monomer concentration can be assumed to be constant at low conversion. It follows that at two arbitrary CCTA concentrations, 1 and 2, from eq 8, the relative radical concentrations can be equated to the relative rates of polymerization. If a *pseudo* steady state is assumed for the radical concentration, then, in the absence of inhibition or retardation, the rate of termination can be equated to the rate of initiation, yielding eq 9.

$$\langle k_t\rangle = R_I/[\mathrm{R}^\bullet]^2 \quad (9)$$

From this equation and the above assumptions, it follows that the termination rate coefficients at the two CCTA concentrations 1 and 2 are related by eq 10.

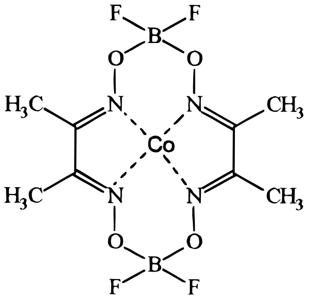
$$\frac{\langle k_t\rangle_1}{\langle k_t\rangle_2} = \frac{[\mathrm{R}^\bullet]_2^{\,2}}{[\mathrm{R}^\bullet]_1^{\,2}} = \left(\frac{R_{p2}}{R_{p1}}\right)^2 \qquad (10)$$

The relative termination rate coefficients can then be plotted as a function of number-average degree of polymerization using this equation.

It is generally assumed that segmental and center-of-mass diffusion are the dominant termination mechanisms at low conversions. Based on this, an expression has been proposed for the dependence of the termination rate coefficient on number-average degree of polymerization.[15]

$$\langle k_t\rangle \sim \mathrm{DP}_n^{\;a} \qquad (11)$$

The parameter a is predicted to vary between −0.5 for short chain lengths (less than ca. 100) and −0.1 for long chains.



1 COBF

Throughout this work the CCTA used is COBF, **1**, ([bis[μ-[(2,3-butanedione dioximato)(2−)-*O*,*O*′]]tetrafluorodiborato(2−)-*N*,*N*′,*N*″,*N*‴] cobalt). It is studied in the polymerization of MMA both in toluene solution and in the absence of solvent, bulk, and in the polymerization of styrene in the absence of solvent. One objective of this work is to ascertain the most appropriate method for obtaining chain transfer constants for CCTP, and thus the best method of quantifying CCTA efficiency. The use of SEC and MALDI-TOF are compared as are the Mayo equation and number distributions method of determining C_S. Furthermore, the chain length dependence of the average termination rate constant is also examined in light of eq 10.

Experimental Section

Table 1 summarizes the composition of the reaction mixtures for the experiments discussed. The three series A, B, and C correspond to the polymerization of methyl methacrylate in toluene solution, methyl methacrylate in the absence of solvent, and styrene in the absence of solvent, respectively.

All reactions were carried out using standard Schlenk apparatus and closed ampules in a 60 °C (±0.5 °C) constant-temperature water bath. The reaction mixtures were deoxygenated by freeze−pump−thaw. Methyl methacrylate was obtained from ICI and passed down a column containing basic alumina and 3 Å molecular sieves under nitrogen prior to use. Styrene was obtained from Aldrich and passed down a basic alumina column and deoxygenated by bubbling with nitrogen for 60 min prior to use. Toluene was distilled from sodium under nitrogen, and AIBN was obtained from BDH and recrystallized from methanol. The COBF was prepared according to the method of Espenson[16] and recrystallized from methanol to yield the bismethanol adduct as opposed to the bisaqua complex. COBF can be difficult to characterize and purify, so a single batch was used throughout this work.

Table 1. Composition of Polymerization Reactions

run	monomer	monomer (mL)	solvent	solvent (mL)	AIBN (mg)	[COBF]/[monomer] × 10^9
A1	MMA	2.00	toluene	4.00	10.0	0
A2	MMA	2.00	toluene	4.00	10.0	261.0
A3	MMA	2.00	toluene	4.00	10.0	522.0
A4	MMA	2.00	toluene	4.00	10.0	1044
A5	MMA	2.00	toluene	4.00	10.0	2088
B1	MMA	5.00			25.0	0
B2	MMA	5.00			25.0	23.73
B3	MMA	5.00			25.0	47.46
B4	MMA	5.00			25.0	94.93
B5	MMA	5.00			25.0	189.9
C1	STY	4.00			20.0	0
C2	STY	4.00			20.0	5106
C3	STY	4.00			20.0	10212
C4	STY	4.00			20.0	15318
C5	STY	4.00			20.0	20423

Stock solutions of initiator in monomer and COBF in monomer (or toluene for series A) were prepared. The appropriate amount of each stock solution was added to an ampule fitted with a Young's vacuum tap. The monomer and, where used, solvent were then added. A final deoxygenation was conducted using freeze−pump−thaw. The reaction mixtures were then immersed in a constant-temperature water bath for 15 min in the case of the two bulk polymerization series (B and C) or 30 min for the solution polymerizations (series A). For each series a set of five separate experiments was carried out; four different [COBF]/[monomer] levels and one control experiment containing no COBF. All were prepared using identical stock solutions.

Typical Polymerization Procedure. A stock solution of COBF was prepared by dissolving 2.2 mg of COBF in 50 mL of toluene. A second initiator stock solution was prepared by dissolving 60 mg of AIBN in a mixture of 12 mL of MMA and 18 mL of toluene. Five reaction mixtures were prepared, each containing 5 mL of the initiator solution and a mixture of toluene and the COBF stock solution totaling 1 mL. The amounts of COBF stock solution used in the five reactions were 0, 0.05, 0.10, 0.20, and 0.40 mL. After being deoxygenated and sealed, all five reactions were heated simultaneously at 60 °C for 15 min prior to being cooled in ice. SEC was carried out on the reaction mixture to avoid fractionation on precipitation. Yields were determined by drying a known weight of the reaction mixture to constant weight in a vacuum oven at 60 °C, typically for 48 h.

SEC was carried out with a Polymer Laboratories PL-guard column (50 × 7.5 mm), 2 PL-Mixed-C columns (300 × 7.5 mm), and a differential refractive index detector. THF was used as the eluent at a flow rate of 1 mL/min and data were collected at 1 point per second. The system was calibrated with log(molecular weight) expressed as a third-order polynomial of elution volume based on calibrants of the same polymer as was being analyzed. For poly(methyl methacrylate), 10 Polymer Laboratories PMMA standards with peak molecular weights between 1140 and 1 577 000 and pure MMA dimer and trimer were used. For polystyrene, 10 Polymer Laboratories PS standards with peak molecular weights between 580 and 3 150 000 were used.

MALDI-TOF mass spectrometry was carried out on a Kratos Kompact III spectrometer in reflectron mode. This instrument uses a 337 nm nitrogen laser with a 3 ns pulse duration for ionization and an electron multiplier detector. 2,5-Dihydroxybenzoic acid doped with sodium acetate was used as the matrix. It was deposited from acetone solution onto the stainless steel sample substrate and the solvent allowed to evaporate. The polymer was then deposited as a dilute (~1 mg/mL) solution in THF. This resulted in each polymeric species being observed as its Na^+ adduct with molecular mass $M + 23$. The spectrometer was calibrated using bovine insulin (5734) and sodium (22.9898).

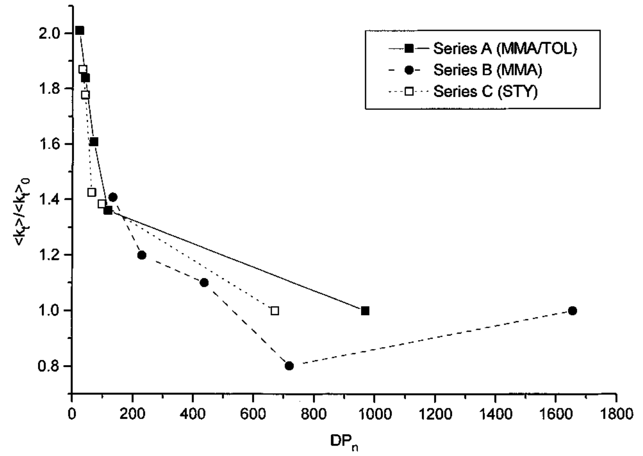


Figure 1. Relative average termination rate coefficients plotted as a function of degree of polymerization.

Table 2. Summary of the Molecular Weight Average and Conversion Data

run	M_n	PDI	% conv
A1	97019	2.046	7.43
A2	11822	2.026	6.37
A3	6980	1.986	5.86
A4	4173	1.902	5.48
A5	2210	1.709	5.24
B1	165602	1.886	6.80
B2	71979	2.198	7.59
B3	43733	2.202	6.48
B4	23001	1.198	6.21
B5	13311	2.148	5.73
C1	69886	1.876	1.60
C2	10118	2.416	1.36
C3	6604	2.122	1.34
C4	4376	2.123	1.20
C5	3441	2.132	1.17

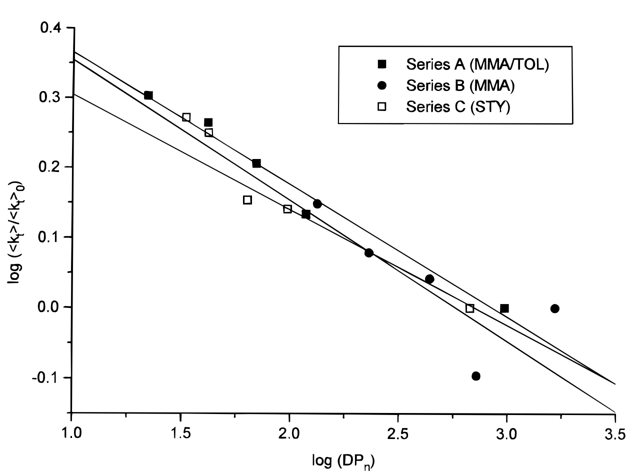


Figure 2. Relative average termination rate coefficients plotted in the form of eq 11 showing the lines of best fit.

Table 3. Parameters Describing the Chain Length Dependence of the Termination Rate Constant from Figure 2

series	a	$\log(\langle k_t\rangle^1/\langle k_t\rangle_0)$
A	−0.189 ± 0.032	0.555 ± 0.064
B	−0.165 ± 0.157	0.469 ± 0.419
C	−0.201 ± 0.059	0.555 ± 0.118

Results and Discussion

Table 2 summarizes the conversion and molecular weight average data for the polymerizations discussed in this work. These polymerizations were all conducted at relatively low conversions and cover a wide range molecular weights. These experiments were primarily designed to study chain transfer and not termination. However, the wide range of molecular weights produced under identical initiation and propagation conditions along with the similar polydispersities within a series makes these data useful for examining the chain length dependence of the termination rate coefficient. If the assumptions used to derive eq 10 hold, then (since these are at relatively low conversion and within a series all of the polymerizations were carried out for the same time) we can use the conversion data as polymerization rate data in eq 10. Figure 1 is a plot of the relative termination rate coefficients as a function of degree of polymerization for the three series of polymerizations examined in this work. The polymerizations in the absence of COBF (i.e. A1, B1, and C1 with $DP_n = 969$, 1654, and 671, respectively) were used as the reference conditions and the term $\langle k_t\rangle_0$ refers to these conditions. It is well recognized that the CT reaction in CCTP between a monomeric radical and the CCTA produces monomer. As such, this reaction is not perceived by the analysis of the product polymer. When large amounts of monomer-producing reactions occur, as is the case at very high CCTA concentrations where low-M_n products formed, the generation of monomer manifests itself as a flattening (decrease in slope) in the Mayo plot at high [S]/[M]. However, the lowest MW sample used in the study had $DP_n = 22$. Even under these conditions the influence of “monomer generation” by CCT is expected to be small. Based on the number distribution data for this sample (partially illustrated in Figure 4), monomeric product would be expected to amount to approximately 5 mol % of the total product. In terms of weight this product is expected to contribute much less, on the order of 1 wt %. Since eq 10 relates the relative termination rate coefficients to weight (through R_p as determined by gravimetry), it is insensitive to “monomeric product” under the conditions used in this work. A clear chain length dependence is observed for each of the three series. The relative termination rate coefficient decreases with chain length. Following from eq 11, a plot of the logarithm of the relative rates versus the logarithm of the number-average degree of polymerization will give a line with slope *a* and an intercept equal to the logarithm of ratio of termination coefficient at number-average degree of polymerization equal to 1 to that of the reference conditions (i.e. $\log(\langle k_t\rangle^1/\langle k_t\rangle_0)$). The data are plotted in this form in Figure 2 and the values determined from the line of best fit are included in Table 3. Although there is a large amount of uncertainty associated with these values (as indicated by the 95% confidence intervals), the exponents *a* fall within the theoretically predicted limits for diffusion (center of mass and segmental) controlled termination (eq 11) and are similar for the three different polymerization conditions. It appears that the chain length dependence of termination is similar in the polymerization of MMA in the bulk and in toluene solution and that a similar dependence is found for styrene in the bulk. The values of the intercepts suggest that for these runs the termination rate coefficients at degree of polymerization equal to 1 are approximately 3−4 times larger than under the arbitrary reference conditions defined above.

Number Distributions from MALDI-TOF and SEC. Since MALDI-TOF mass spectrometry analysis of a polymer should give the number distribution of the polymer directly, it would obviously be the technique

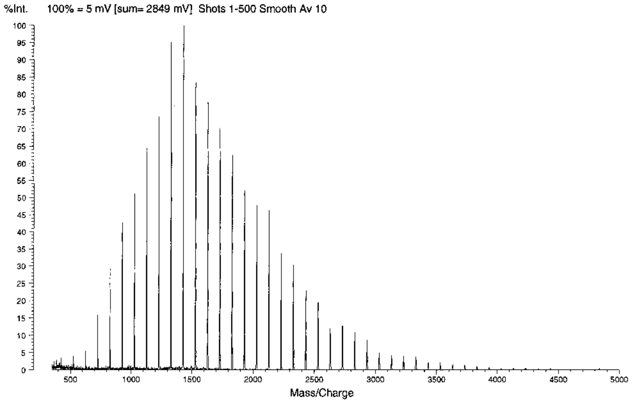


Figure 3. MALDI-TOF spectrum of the reaction product from polymerization A5.

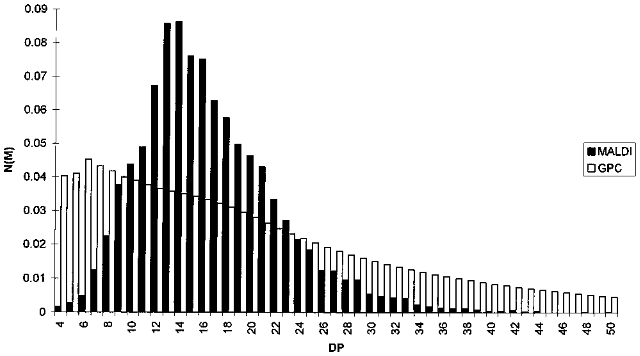


Figure 4. Comparison of the number distributions obtained from SEC and MALDI-TOF analysis of the product from reaction A5.

of choice for polymer characterization to use with the number distribution technique for determining chain transfer constants. Inspection of a MALDI-TOF spectrum for the polymer A5 used in this work (Figure 3) reveals that this analysis gives the incorrect number distribution. The spectrum is clearly not dominated by an exponential decay as would be expected for the number distribution of this type of polymer based on theory. In contrast, the (discrete) number distribution obtained from SEC (corrected for the chain length dependence of refractive index) agrees quite well with the form predicted by theory as can be seen in Figure 4, where the number distributions from the two different techniques are compared. It is known that MALDI-TOF currently suffers from a number of limitations with regard to mass sensitivity which can lead to large errors in molecular weight averages determined from this new technique.[17,18,19] The mass envelope in the spectrum shown in Figure 3 discriminates against *both* low- and high-mass macromolecules. Here it shown that MALDI-TOF under the conditions used here gives the wrong general shape for the distribution. Comparison of the number distribution obtained from mass spectrometry techniques and size exclusion chromatography may give valuable insights into the nature of these deviations. Here the deviation is likely due in large part to a chain length sensitivity of the ionization in MALDI-TOF. If this is the case, then Figure 5, which plots the ratio of the number distribution from MALDI-TOF to that from the SEC, is presumably a plot of the relative ionization efficiency in MALDI-TOF. However, at present, the mass sensitivity of MALDI-TOF mass spectrometry is currently not well understood and it is not the purpose of this work to explore this further. Obtaining the correct number distribution, especially for polymers with broad molecular weight distributions, from MALDI-TOF is not currently routine. Thus the average molecular weights and number distributions in the rest this work refer to those obtained by SEC.

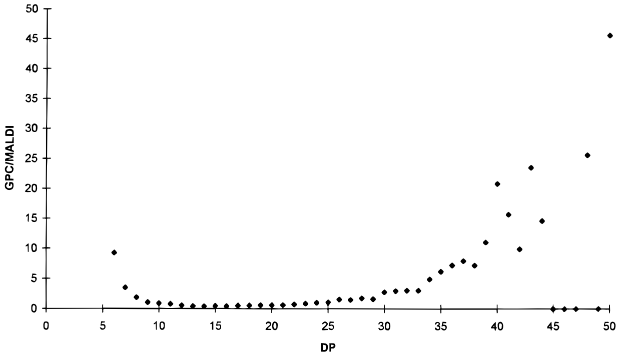


Figure 5. Plot of the ratio of the number distribution from MALDI-TOF to that from SEC, indicating the mass sensitivity of MALDI-TOF.

Use of the Number Distribution and Mayo Equation for Evaluating Chain Transfer Constants. The two general methods of evaluating chain transfer efficiencies, the Mayo equation, and the use of the number distribution were compared. A total of five procedures which were variations of the two methods were implemented.

Procedure 1: This procedure is probably the most widely used implementation of the Mayo equation (eq 2), the use of a Mayo plot. A linear regression was performed on the experimental data in the form of $1/\mathrm{DP}_n$ against [S]/[M]. The slope of this line of best fit equates to the chain transfer constant.

Procedure 2: This procedure is a second variation on the use of the Mayo equation. C_S is evaluated for each of the samples containing chain transfer agent by solving the Mayo equation in the form $C_S = ([\mathrm{M}]/[\mathrm{S}])(1/\mathrm{DP}_n - 1/\mathrm{DP}_{n0})$. The experimental values of $1/\mathrm{DP}_n$ and $1/\mathrm{DP}_{n0}$ were used.

Procedures 1 and 2 assume that the rate of polymerization is not affected by the addition of the chain transfer agent. The conversion data in Table 2 indicate that this is not the case for these polymerizations. The chain length dependence of the termination reaction makes it necessary to consider the consequences of the violation of this assumption. The term in parentheses in eq 3 equates to the inverse of the number-average chain length in the absence of chain transfer agent. This is the only term in the Mayo equation which depends on the rate of polymerization, and this term will not be constant for polymerizations performed under identical conditions (except for chain transfer agent level) having different polymerization rates. Any effects of the rate of polymerization manifest themselves through this term. Assuming that the nature of termination (i.e. F_c) remains constant, this term can be recast in a form which shows its dependence on the rate of polymerization, eq 12. The terms α and β will remain constant in polymerizations performed under the same conditions with the same rate of initiation. The first term of eq 12 represents the reciprocal of the average degree of polymerization which would be produced in the absence of any chain transfer reactions and thus depends on the rate of initiation of kinetic chains to the rate of propagation. The term β represents the contribution resulting from chain transfer to monomer, initiator, and solvent.

$$\frac{1}{\mathrm{DP}_{\mathrm{n0}}} = \frac{\alpha}{R_{\mathrm{p}}} + \beta \qquad (12)$$

Two limiting cases are important in determining the effect of the rate of polymerization. These expressed in the form of eq 12 are (i) the case where chain transfer to monomer, initiator, and solvent determine $\mathrm{DP}_{\mathrm{n0}}$, $\beta \gg \alpha/R_{\mathrm{p}}$, and (ii) the case where chain transfer has a negligible effect on $\mathrm{DP}_{\mathrm{n0}}$, $\alpha/R_{\mathrm{p}} \gg \beta$. All systems will behave within the limits imposed by these two cases. Consider two polymerizations A and B performed under identical conditions except for the level of chain transfer agent. The number-average degrees of polymerization expected in the absence of chain transfer agent can be related by eq 13.

$$\frac{\mathrm{DP}^{\mathrm{B}}_{\mathrm{n0}}}{\mathrm{DP}^{\mathrm{A}}_{\mathrm{n0}}} = \frac{\alpha/R^{\mathrm{A}}_{\mathrm{p}} + \beta}{\alpha/R^{\mathrm{B}}_{\mathrm{p}} + \beta} \qquad (13)$$

$$\frac{\mathrm{DP}^{\mathrm{B}}_{\mathrm{n0}}}{\mathrm{DP}^{\mathrm{A}}_{\mathrm{n0}}} = \frac{R^{\mathrm{B}}_{\mathrm{p}}}{R^{\mathrm{A}}_{\mathrm{p}}} \qquad (14)$$

It can be seen that if case i holds for both polymerizations, then the rate of polymerization will not affect the chain transfer coefficient; the number-average degree of polymerization will not change with the rate of polymerization. In the limit of the molecular weight being dominated by chain transfer to monomer, initiator, and solvent, the right-hand term of eq 13 equals 1. Case i polymerizations can be handled using the standard Mayo treatments (i.e. procedures 1 and 2).

In the limit where case ii holds for both polymerizations, eq 13 reduces to eq 14. The expected degrees of polymerization in the absence of added chain transfer agent are proportional to the rate of polymerization. In practice, this means that case ii polymerization systems having significant changes in rate will exhibit concave Mayo plots since the rate of polymerization is not taken into account. It will result in overestimation of the chain transfer constant from the use of eq 2. The change in polymerization rate in a case ii system can by accounted for through eq 14, if a control polymerization is conducted without added chain transfer agent. The $\mathrm{DP}_{\mathrm{n0}}$ at each level of chain transfer agent can be calculated from the rate of polymerization (or conversion for low-conversion polymerizations) relative to the control and the $\mathrm{DP}_{\mathrm{n0}}$ of the control.

The polymerization conditions used to produce the polymers in this work fall between the two limiting cases of eq 13. An approximate value β was calculated for the control polymerizations using literature values for the chain transfer constants to monomer, initiator, and solvent where applicable ($C_{\mathrm{M,MMA}} = 1 \times 10^{-5}$, $C_{\mathrm{toluene,MMA}} = 2 \times 10^{-5}$, $C_{\mathrm{AIBN,MMA}} = 2 \times 10^{-2}$, $C_{\mathrm{M,STY}} = 6 \times 10^{-5}$, $C_{\mathrm{AIBN,STY}} = 0.14{-}0.091$).[5,7] These calculations show effects of chain transfer to monomer, initiator, and solvent (the term β) are neither dominant nor negligible in all cases. The behavior of these systems will be between the limits defined by cases i and ii. Procedures 1 and 2 apply to case i systems. Procedure 3 is developed for case ii systems.

Procedure 3: This procedure is a third variation on the use of the Mayo equation which applies to case ii systems. As with procedure 2, C_{S} is evaluated for each of the samples containing chain transfer agent by solving the Mayo equation in the form $C_{\mathrm{S}} = ([\mathrm{M}]/[\mathrm{S}])(1/\mathrm{DP}_{\mathrm{n}} - 1/\mathrm{DP}_{\mathrm{n0}})$. The experimental values of $1/\mathrm{DP}_{\mathrm{n}}$ are used. However, $1/\mathrm{DP}_{\mathrm{n0}}$ is calculated for each sample from its conversion data and the conversion and degree of polymerization of the control polymerization (no COBF) using eq 14. By doing so, the variation in the rate of polymerization that occurs with the level of chain transfer agent is accounted for.

In practice, for polymerizations where the addition of a chain transfer agent affects the rate of polymerization, both procedures 2 and 3 should be used to determine the chain transfer activity. These serve as upper and lower limits for the true chain transfer activity.

Procedure 4: This is the conventional treatment of the number distribution data. For a series of polymerizations with differing [S]/[M] ratios, the line of best fit is determined for the linear region of a plot of $\ln(N(\mathrm{DP}))$ versus DP. These slopes are then plotted against the [S]/[M] ratio and the line of best fit determined. The slope of this line equates to C_{S} and the intercept corresponds to the other terms in the eq 4.

Procedure 5: This is an alternative way of examining the number distribution data. One factor which complicates the use of the number distribution for determining C_{S} values is that it is the superposition of the distributions generated by all chain-breaking reactions. The contributions from reactions other than chain transfer to added chain transfer agent are significant but diminish as the level of added chain transfer agent is increased (see Figures 11, 15, and 19). Since only the primary chain transfer reaction is of interest, it would be desirable to obtain data under conditions where other reactions make a negligible contribution. Procedure 5 is an attempt to ovecome the difficulties associated with these other chain reactions by extrapolating into the region where they are not important. Equation 4 can be recast as eq 15 with the term A containing the effects of all chain-breaking reactions other than chain transfer to the added chain transfer agent. From eq 15, it can be expected that a plot of $\ln(N(\mathrm{DP}))[\mathrm{M}]/[\mathrm{S}]$ versus DP will be revealing. Such plots will have a linear region with a slope of $-(A([\mathrm{M}]/[\mathrm{S}]) + C_{\mathrm{S}})$. This can be plotted against [M]/[S] for a series of polymerizations with different levels of chain transfer agent. The physical meaning of such a plot is clear: as the ratio [M]/[S] approaches zero, the level of chain transfer agent relative to monomer approaches infinity. Thus the polymerization must become dominated by chain transfer in this region. C_{S} can be determined from the intercept obtained by extrapolating a plot of $(A([\mathrm{M}]/[\mathrm{S}]) + C_{\mathrm{S}})$ versus [M]/[S] to zero.

$$N(\mathrm{DP}) = \exp\left(-\left(A + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]}\right)\mathrm{DP}\right) \qquad (15)$$

Procedure 5 obtains slopes from the linear regions of plots of $\ln(N(\mathrm{DP}))[\mathrm{M}]/[\mathrm{S}]$ versus DP by linear regression. These slopes are then plotted against [M]/[S]. In procedure 5 the line of best fit is determined and the intercept equated to C_{S}. Although not discussed further here, these plots may be valuable in the study of termination reactions. The true shape of these plots of slope against [M]/[S] is of interest. The term A contains information on termination through $\langle k_{\mathrm{t}}\rangle[\mathrm{R}^{\bullet}]$ and on the other chain-breaking reactions through $k_{tr,\mathrm{M}}[\mathrm{M}]$, and $\sum k_{tr,\mathrm{C}}[\mathrm{C}]$. The termination component will vary with [M]/[S] while the other components remain constant for a polymerization series.

Polymerization series A consisted of a series of catalytic chain transfer polymerizations of methyl meth-

Table 4. Chain Transfer Constants and Slopes (See Text) Determined

run[a]	C_S procedure 1	C_S procedure 2	C_S procedure 3	C_S procedure 4	−slope procedure 5
A2		28490	27840		30850
A3		25500	24970		29190
A4		21990	21640		27760
A5		21200	21000		25430
avg	20700 ± 1350	24300 ± 6730	23860 ± 6340	24870 ± 1110	25710 ± 1734
B2		33140	35790		62590
B3		35500	34870		52650
B4		39480	38880		46972
B5		36420	35830		38418
avg	36940 ± 2180	36140 ± 5250	36340 ± 3500	34780 ± 3010	38250 ± 5250
C2		1724	1670		1927
C3		1398	1370		1769
C4		1456	1420		1682
C5		1409	1380		1657
avg	1390 ± 100	1500 ± 310	1460 ± 280	1540 ± 25	1570 ± 30

[a] Avg refers to average or estimate from linear regression. In column 6 it refers to the intercept obtained by extrapolating into the chain transfer dominated regime according to procedure 5.

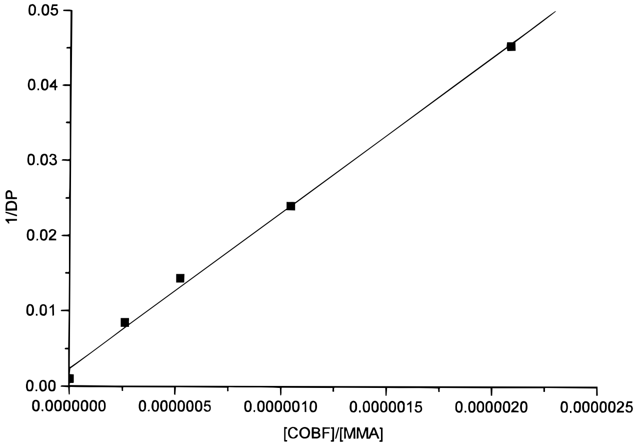


Figure 6. Mayo plot for polymerization series A, the COBF-modified polymerization of MMA in toluene solution.

acrylate in toluene solution. The data relevant to the Mayo treatment of the data are found in Tables 1 and 2. Figure 6 is a Mayo plot for these experiments. The data are well described by eq 2, showing the expected dependence of number-average degree of polymerization on the chain transfer to monomer ratio. Procedure 1 yields a value of 20 700 ± 1350 for the chain transfer constant for COBF in these polymerizations. The C_S values determined by procedure 2 are presented in Table 4. The average value from procedure 2 is 24 300 ± 6730. The use of procedures 1 and 2 assumes that the rate of polymerization does not need to be considered; it is either constant or the system follows case i behavior as described above. The C_S values obtained using procedure 3, which assumes case ii behavior, are given in Table 4. For this series of polymerizations the average value is 23 860 ± 6340. Procedures 2 and 3 give values representing the two limiting cases i and ii, respectively, which are within 3% of each other. This indicates the effect of changes in the rate of polymerization is a small one in these polymerizations. This observation is further supported by the fact that the Mayo plot is not concave, as would be expected if the change in polymerization rate had a strong influence.

The number distributions (all normalized to the same area) for the polymers in series A are plotted in Figure 7a,b. As anticipated from eq 4, these distributions are dominated by an exponential decay at all but very low degrees of polymerization. Figure 7a shows the data for all of the samples plotted on the same scale. Here the expected effect of the level of chain transfer agent is observed: the number distributions show a more rapid decay as the level of chain transfer agent is increased. Inspection of Figure 7a also reveals that the decay occurs on a very different scale for the sample containing no added chain transfer agent. Its number distribution is plotted separately in Figure 7b. Figure 8 is a partial plot of ln(N(DP)) versus DP for the control samples (no COBF) for the three polymerization series. A linear region at relatively low degrees of polymerization is exhibited for each of these polymerizations. In the control polymerization the low molecular weight region is not transfer dominated; it is termination dominated. However, since these samples are relatively

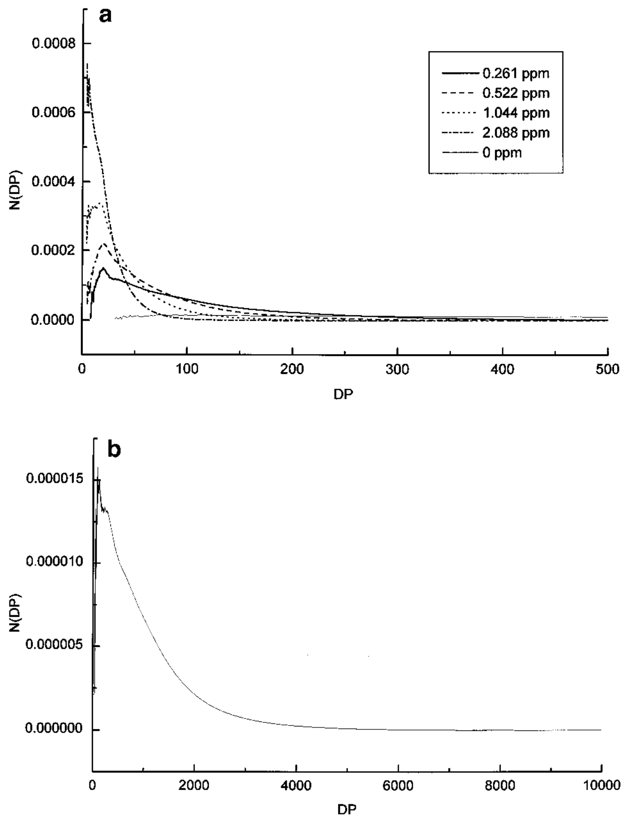


Figure 7. Number distributions of the products from polymerization series A: (a) all samples in the series; (b) the control sample A1, which contained no COBF.

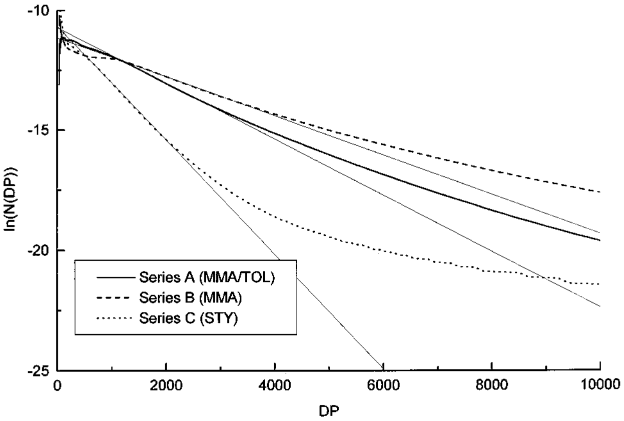


Figure 8. Plot of the number distribution in the form of the logarithm of the relative number of polymer chains, ln(N(DP)), as a function of degree of polymerization for the control samples (A1, B1, and C1 containing no COBF) for each of the three polymerization series.

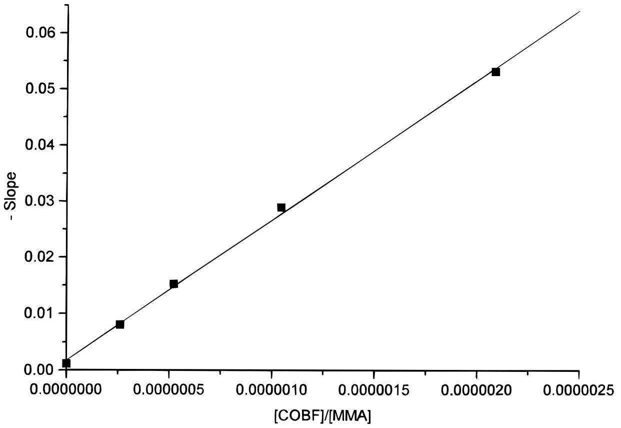


Figure 9. Plot of the slope of the linear regions of ln(N(DP)) vs DP against the mole ratio of COBF to monomer for series A.

low molecular weight (M_n ca. 100K), even the high molecular weight slope is dominated by termination, not transfer, and is therefore also not particularly useful in the analysis. Most of the work done to date with the number distributions has dealt with emulsion polymers in order to produce high enough molecular weights to examine chain transfer to monomer. The use of the high molecular weight slope in this context is not yet fully established. Since the control samples are included in the analysis for procedure 4 (i.e. they are used as a point in the regression; see Figures 9, 13, and 17), they will have a (small) effect on the C_S value that is obtained. Termination obviously complicates this type of analysis. The slope used for all of the other samples is the low molecular weight slope. This is used since it contains information on the complicating reactions (e.g. termination) in the region of interest. The line of best fit for the linear region of each of these plots is represented by the thin solid line. Similar plots were obtained for all of the polymerizations in series A and the slopes of the linear regions were used to determine C_S as described in procedure 4. Figure 9 is a plot of the data in the form used to estimate C_S in procedure 4. The line of best fit gives a slope corresponding to a C_S value of 24 870 ± 1110, in excellent agreement with the values obtained by the Mayo treatments, particularly procedures 2 and 3, where there was less than 5% discrepancy.

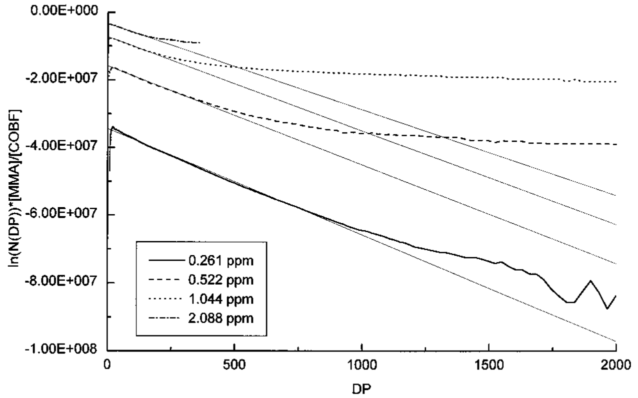


Figure 10. Modified plot of the number distribution ln(N(DP))[M]/[S] vs degree of polymerization for the polymerizations in series A containing COBF (A2−A5).

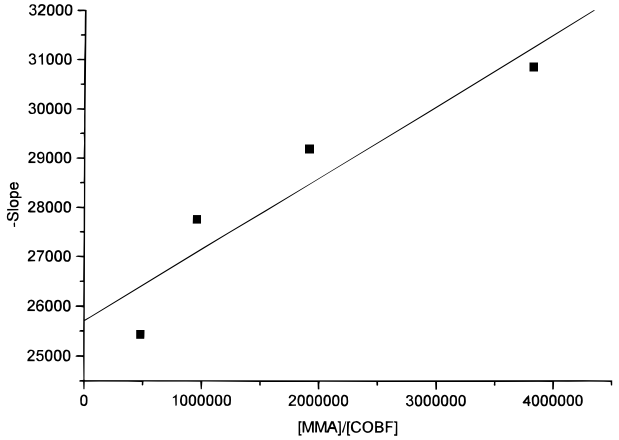


Figure 11. Plot of the slope of the linear regions of ln(N(DP))[M]/[S] vs DP against the mole ratio of monomer to COBF for polymerizations A2−A5.

Figure 10 shows plots of ln(N(DP))[M]/[S] versus DP for the polymerizations in series A which contained COBF. It can be seen that each of these plots has a linear region at relatively low degree of polymerization and that these linear regions are nearly parallel, in accord with eq 15. Following procedure 5, the lines of best fit determined by linear regression in these regions are represented by the thin solid lines in Figure 10. The slopes of these lines are contained in Table 4. The slopes of these lines are quite close to, but slightly higher than, the values of the C_S obtained from the earlier treatments of the same data set. The slopes vary between 30 850 and 25 430 and show a decrease with increasing levels of COBF. This is a result of the contribution from termination and other chain transfer reactions diminishing as the level of CCTA is increased. For each sample, the regression was performed over the same range of degrees of polymerization as was used to determine the line of best fit in the ln (N(DP)) versus DP plots in procedure 4. The next step in procedure 5 takes the slopes as determined above and plots them versus [M]/[S] (Figure 11). This plot is then extrapolated to [M]/[S] equal to zero. A straight line was fitted to these data, yielding an intercept 25 710 ± 1730. Procedure 5 yields a C_S value which is in good accord with the values obtained from the Mayo treatment of the data and with the conventional treatment of the number distribution.

These polymerizations were *not* conducted under conditions with low radical concentration (approaching the limit of zero initiator concentration). As such, the normal chain-breaking reactions such as normal termi-

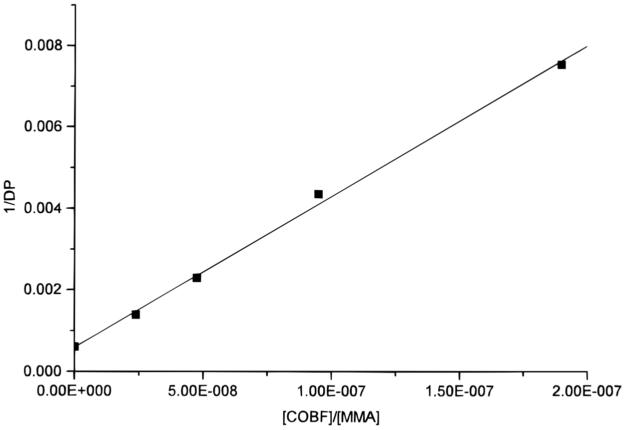


Figure 12. Mayo plot for polymerization series B, the COBF-modified polymerization of bulk MMA.

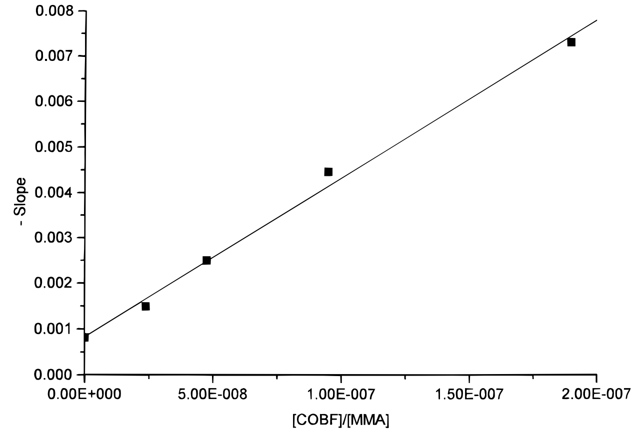


Figure 13. Plot of the slope of the linear regions of ln(N(DP)) vs DP against the mole ratio of COBF to monomer for series B.

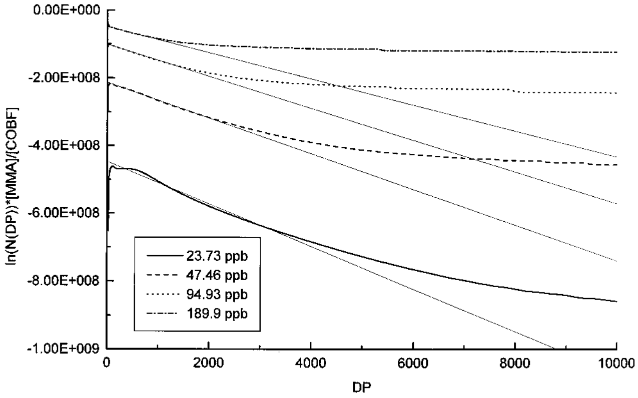


Figure 14. Modified plot of the number distribution ln(N(DP))[M]/[S] vs degree of polymerization for the polymerizations in series B containing COBF (B2–B5).

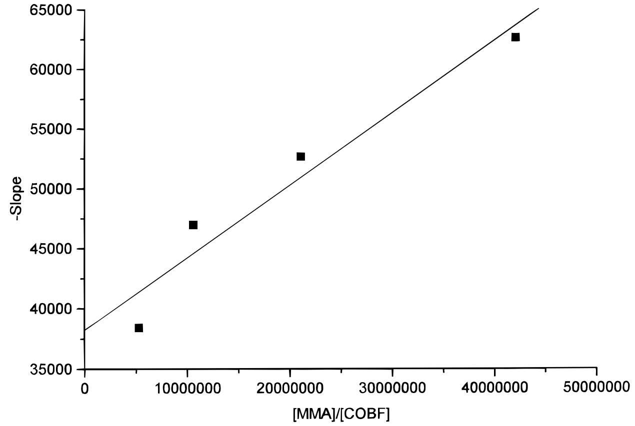


Figure 15. Plot of the slope of the linear regions of ln(N(DP))[M]/[S] vs DP against the mole ratio of monomer to COBF for polymerizations B2–B5.

nation cannot be neglected. The decrease in slope observed with increasing amounts of COBF is consistent with this since the effects of these other reactions will be diminished as more chain transfer to the chain transfer agent occurs. In eq 4, the term $k_{tr,s}$[S] will only be large relative to the sum of $k_{tr,\mathrm{M}}$[M], $\langle k_t \rangle$[R$^\bullet$], and $\sum k_{\mathrm{tr,C}}$[C] when chain transfer to added chain transfer agent is the dominating chain-breaking event. Comparison of the number-average molecular weights made in the presence and absence of added chain transfer can serve as a measure of the significance of normal termination and other transfer reactions. In this series the runs containing COBF produced between 8.2 and 43.9 times more chains than were produced in the absence of COBF. Clearly, these other reactions are significant, particularly at the lower levels of chain transfer agent. This complicates the use of the number distribution for determining chain transfer constants under many conditions, necessitating extrapolation into regimes where these other chain-breaking reactions can be neglected.

Series B is a set of catalytic chain transfer polymerizations of methyl methacrylate performed in bulk. Figure 12 is a Mayo plot for this series (the data are contained in Table 2) and again the expected linear relationship between the reciprocal of the number-average degree of polymerization and mole ratio of chain transfer agent to monomer is observed. The slope of the line (procedure 1) corresponds to a C_S value of 36 940 ± 2180, and the chain transfer constant estimated from procedure 2 is 36 130 ± 5250. These represent the upper limit to C_S; case i behavior is assumed. Procedure 3, the treatment of the data which corresponds to the other limiting behavior, case ii, gives a C_S value of 36 340 ± 3500. Here the case ii value is larger than the case i value because of the conversion data for sample B2. The number distributions for series B are also dominated by an exponential decay. Procedure 4 gives a C_S value of 34 780 ± 3010 (Figure 13). Again the value obtained from the conventional treatment of the number distribution is in excellent agreement with the value obtained from the Mayo treatment. The number distribution data for series B were also used with procedure 5. As with series A, in the low molecular weight region each of the samples displays a linear region in the ln(N(DP))[M]/[S] versus DP plots (Figure 14). The slopes of all of these regions (represented by the thin solid lines in Figure 14) are nearly parallel and are given in column 6 of Table 4. Again, these slopes are very similar to the chain transfer constants determined from the Mayo equation. They show the same trend as series A, showing decreasing slope with increasing COBF level. These slopes are plotted as a function of [M]/[S] in Figure 15. Extrapolation to the chain transfer dominated region using linear regression yielded a value of 38 250 ± 5250. The number-average molecular weight data for this series indicate that termination should not be ignored when considering the number distributions for series B. In these polymerizations chain transfer only increased the number of chains by a factor of between 2.3 and 12.4. Hence the importance of the intrinsic chain-breaking events relative to chain transfer (i.e. the sum $k_{tr,\mathrm{M}}$[M] + $\langle k_t \rangle$[R$^\bullet$] + $\sum k_{tr,\mathrm{C}}$[C] relative to $k_{\mathrm{tr,s}}$[S]) is larger in these

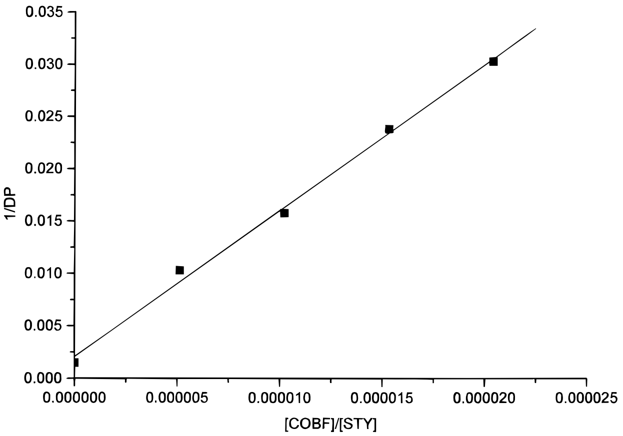


Figure 16. Mayo plot for polymerization series C, the COBF-modified polymerization of bulk STY.

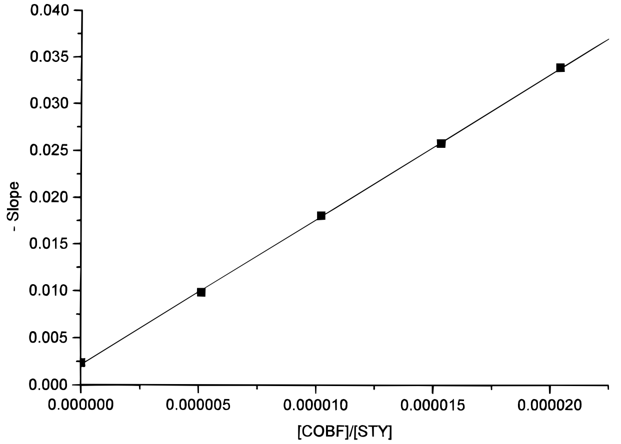


Figure 17. Plot of the slope of the linear regions of ln(*N*(DP)) vs DP against the mole ratio of COBF to monomer for series C.

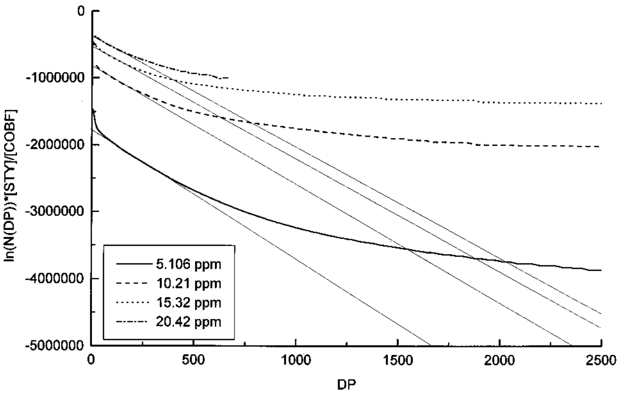


Figure 18. Modified plot of the number distribution ln-(*N*(DP))[M]/[S] vs degree of polymerization for the polymerizations in series C containing COBF (C2−C5).

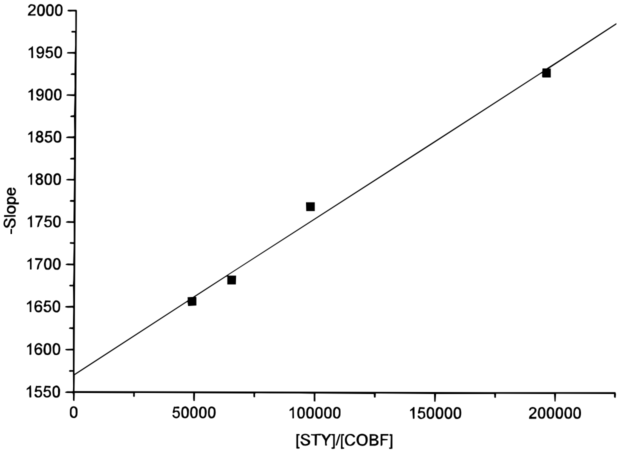


Figure 19. Plot of the slope of the linear regions of ln(*N*(DP))-[M]/[S] vs DP against the mole ratio of monomer to COBF for polymerizations C2−C5.

polymerizations than in series A. These C_S values obtained from these bulk polymerizations are in good accord with literature values of 40 400 for COBF in the bulk polymerization of MMA under similar conditions.[20] The C_S values obtained from the polymerizations of MMA in toluene solution, series A, and in bulk, series B, differ by a factor of 1.5. A strong solvent effect is demonstrated. Other reports of solvent effects with COBF have been reported in the literature, including an extreme case where it behaved as a catalytic inhibitor.[6,21]

Series C is a bulk polymerization of styrene containing COBF as a chain transfer agent. It behaves similarly to the other two series and the data are treated in the same manner. Figure 16 is the Mayo plot for series C. Procedures 1 and 2, both of which assume case i behavior, yield C_S values of 1390 ± 100 and 1500 ± 310, respectively. Procedure 3, which assumes case ii behavior, results in an average C_S value of 1460 ± 280. Procedure 4 gives a value of 1540 ± 25 (Figure 17). Procedure 5 (Figures 18 and 19) yields an estimate of 1570 ± 30 for the chain transfer constant for COBF in styrene. Again, the C_S values obtained from the number distribution compare favorably with those from the Mayo treatment. The addition of COBF produced between 6.9 and 20.3 times as many chains to be produced, indicating that, as with the previous samples, termination and chain transfer from other sources must be considered. The C_S value for the styrene polymerization is an order of magnitude lower than for MMA. Nonetheless, it is among the highest values of C_S known for styrene and compares favorably with the value of 200 reported for the cobalt complex of hematoporphyrin IX tetramethyl ether, a catalytic chain transfer agent that has been used with styrene.[22] This chain transfer agent is an order of magnitude less active with MMA than COBF (C_S = 2400). Presumably COBF is also more active than the cobalt complex of hematoporphyrin IX tetramethyl ether with styrene.

In the analyses discussed above, three variations on the use of the number-average molecular weights were examined, procedures 1, 2, and 3. Ostensibly, procedures 1 and 2 should give similar values for the chain transfer constant. The average value from procedure 2 and the value from procedure 1 differ by +18, −2, and +8% for series A, B, and C, respectively. Procedures 2 and 3 are the analogous treatments of the data for two limiting behaviors of the polymerizations. These limiting behaviors arise from the sensitivity of the number-average molecular weight of the polymerization product to changes in the rate of polymerization. Procedure 2 assumes that the molecular weight of the polymer is not influenced by the rate of polymerization changing with the level of chain transfer agent, and procedure 3 assumes the maximum sensitivity to changes in the polymerization rate. Procedures 2 and 3 gave results within 3% of each other for all cases except sample B2 (where the conversion was higher than that of the control). This indicates that any effects resulting from changes in polymerization rate with the level of COBF are small in these polymerizations. This being the case, procedures 2 and 3 will not be considered as distinct for comparison of the different methods and the results from procedure 2 will be used.

Procedures 4 and 5 determine the chain transfer constant not from the number average molecular weight but from the shape of the number distribution. It should be noted that the treatments of the number distribution in this work differ from those used previously to obtain chain transfer constants. Previous work has always used the linear region of a ln(N(DP)) versus DP plot in the limit where DP approaches infinity. In this work, the requirement of taking the high molecular weight linear region, as predicted from theory, does not appear to be necessary. Indeed such treatment of the data leads to erroneous results. Although the use of this lower molecular weight linear region lacks the strong theoretical justification behind using the high molecular weight linear region, the method is shown to be sound by the excellent agreement between the C_S values from the number distributions and the Mayo treatments. Further development of the theory applicable to this region is required.

The C_S values obtained from procedures 4 and 5 are in reasonable agreement both with each other and with the values obtained using the number-average molecular weight data. The physical meaning behind procedure 5, extrapolation in to the chain transfer dominated regime, is clearer than that behind procedure 4. However, procedure 4 appears to be the method of choice for analysis of the number distribution data. The slope vs [S]/[M] plot of procedure 4 shows greater linearity than the slope vs [M]/[S] plot of procedure 5, and procedure 4 allows the use of the data from the control run ([S]/[M] equal to zero).

The results from all of the procedures can be compared with each other. The results showing the poorest fit with the other data are those from procedure 1, the use of the Mayo plot. The best agreement occurs between procedures 2 and 4. The average C_S values of these two methods are within 4% of each other, indicating excellent agreement between these two methods even though the two methods use two very different techniques to determine the chain transfer constants. It is worth commenting on the relative merits of the two different methods of determining C_S values as they are based on different assumptions. One uses the shape of the number and thus molecular weight distribution while the other utilizes average molecular weights. These molecular weight averages are determined from the ratios of moments of *the entire molecular weight distribution*. One advantage that has often been cited of the use of the number distribution is its use of the entire molecular weight distribution as opposed to the use of a simple average in the Mayo treatment.[13] This overlooks the fact that molecular weight averages also contain information from the entire molecular weight distribution as the moments are derived from this. Further, the methods which rely on the number distribution use only the fraction of this distribution which has a linear behavior. As a wide range of molecular weights are invariably contained within a polymer sample, this may represent only a small fraction of the material in the polymer (note molecular weight distributions are usually plotted on a logarithmic scale).

Both the number distribution and Mayo methods usually use data derived from SEC. As such, both methods are sensitive to all of the uncertainty associated with this technique. Inaccuracy associated with the peak limit and baseline selection for the chromatogram is particularly relevant as it will affect the two procedures in different ways. Improper peak limits and baseline selection will both cause errors in the average molecular weights used in the Mayo treatment. Number-average molecular weights are particularly sensitive to the low molecular weight region. Errors in the peak limits or baseline in this region will cause significant errors. Furthermore the signal in the low molecular weight region may be complicated by factors such as chain length dependence of refractive index or low molecular weight impurities. The number distribution uses the shape of the distribution. Peak limits are not required, but it is sensitive to baseline selection, particularly in regions with low signal to noise (i.e. the very high and very low molecular weight regions). Improper baseline selection can distort these regions. This will be important in cases where the shape of these regions is of special interest such as determining the chain transfer constant to monomer. The very low molecular weight regions of the chromatogram are generally not of interest in the number distribution procedure. As such, it is immune to the complications which can arise in this region.

It is often seen that the linear region of the plots of the number distribution in the form of ln(N(DP)) versus DP (or ln(N(DP))[M]/[S] versus DP) does not cover the entire molecular weight range.[9,10,11,13] In this work, deviation from linearity is particularly true at the molecular weight extremes. Deviations at the low molecular weight are not unexpected from the theory behind this method; it has been developed for the high molecular weight region. Moreover, complications in the SEC often arise in this region and also contribute. The cause of the deviation exhibited in the higher molecular weight region in this work is unexpected, and the cause is unknown. The deviation at both ends does cause some subjectivity in determining the linear region of the plots. The number distribution, as a method for determining C_S, is somewhat complicated by the fact that it contains so much information. The shape of the distribution is determined by all of the chain-stopping events. This may confound the events due to chain transfer agent. For the polymerizations studied here it was necessary to extrapolate results from several levels of chain transfer agent to conditions which were chain transfer dominated.

There is an underlying assumption in the conventional treatment of number distribution data (procedure 4) that the addition of the chain transfer agent only influences the chain transfer term in eq 4. The conversion data show that the term $\langle k_t \rangle [R^\bullet]$ is also affected by the addition of the chain transfer agent for the polymerizations discussed here. This will influence the plot of slope as a function of chain transfer to monomer ratio in procedure 4. Although the effect appears to be small in this work (by comparison of the calculated intercept with the slope of the sample containing no added chain transfer agent), situations may arise where it may become significant.

There are practical limitations to the use of both the number distribution method and the Mayo treatment for polymerizations involving very active stoichiometric chain transfer agents. Both methods rely on operating the polymerizations under conditions where the [S]/[M] ratio is maintained close to its initial value. For systems with C_S values much greater than 1, this is difficult even for polymerizations taken to low conversion. Integrated forms of the Mayo equation have been developed to account for this.[5] Despite the high C_S values for the chain transfer agent used in this work, the chain transfer was catalytic, allowing these complications to be avoided.

Conclusions

The polymerization series discussed in this work afford polymers with a wide range of molecular weights with similar polydispersities. Within a series, the polymers only differ in the very small amount of CCTA that they contain. This makes these polymerizations well suited for examining the chain length dependence of termination. Methyl methacrylate, both in the bulk and in solution, and styrene in the bulk all showed a strong chain length dependence for average termination rate coefficient. The experimental chain length dependencies were similar for the three polymerization series and fell within the limits predicted from theoretical considerations for diffusion-controlled termination.

The use of MALDI-TOF mass spectrometry and SEC was compared as a means of obtaining number distributions for polymer samples. Currently, MALDI-TOF appears to give number distributions with an incorrect shape. In contrast, SEC appears to give the correct shape, making SEC the current technique of choice for determining number distributions.

Chain transfer constants were determined for COBF using both number-average molecular weights and the shape of number distributions. It is satisfactory that these two very different approaches yield essentially the same values under several polymerization conditions. These two approaches appear to be equivalent for evaluating chain transfer constants.

When number-average molecular weight data were used, the use of a simple Mayo plot (procedure 1) gave values for the chain transfer constant which did not fit in as well as the chain transfer constants determined using procedure 2. Thus procedure 2 is recommended for determining chain transfer constants from number-average molecular weight data. Care should be taken if significant changes in the rate of polymerization occur as the level of chain transfer agent is changed. Procedure 4 appeared to be preferable when number distribution data were used.

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References and Notes

(1) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365.

(2) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243.

(3) Suddaby, K. G.; Haddleton, D. M.; Hastings, J. J.; Richards, S. N.; O'Donnell, J. P. *Macromolecules* **1996**, *29*, 8083.

(4) Kukulj, D.; Davis, T. P.; Suddaby, K. G.; Haddleton, D. M.; Gilbert, R. G. accepted for publication in *J. Polym Sci., Polym. Chem. Ed.* (1996).

(5) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Elsevier Science Ltd.: Tarrytown, NY, 1995.

(6) Haddleton, D. M.; Maloney, D. R.; Suddaby, K. G.; Muir, A. V. G.; Richards, S. N. *Macromol. Symp.* **1996**, *111*, 37.

(7) Odian, G. *Principles of Polymecrization*, 2nd ed.; John Wiley & Sons: New York, 1981.

(8) Rudin, A. *The Elements of Polymer Science and Engineering*; Academic Press: New York, 1982.

(9) Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; 1995, Academic Press: New York, 1995.

(10) Gilbert, R. G. *Trends Polym. Sci.* **1995**, *3*, 222.

(11) Whang, B. C. Y.; Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *Aust. J. Chem.* **1991**, *44*, 1133.

(12) Clay, P. A.; Gilbert, R. G. *Macromolecules* **1995**, *28*, 552.

(13) Christie, D. I.; Gilbert, R. G. *Macromol. Chem. Phys.* **1996**, *197*, 403.

(14) Shortt, D. W. *J. Liq. Chromatogr.* **1993**, *16*, 3371.

(15) O'Driscoll, K. F. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eastmond, G. C., Eds.; Pergamon Press: Elmsford, NY, 1989; Vol. 3, p 161.

(16) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108.

(17) Lloyd, P. M.; Suddaby, K. G.; Varney, J. E.; Scrivener, E.; Derrick, P. J.; Haddleton, D. M. *Eur. Mass. Spectrom.* **1995**, *1*, 293.

(18) Axelsson, J.; Scrivener, E.; Haddleton, D. M.; Derrick, P. J. *Macromolecules* **1996**, *29*, 8875.

(19) Lloyd, P. M.; Scrivener, E.; Maloney, D. R.; Haddelton, D. M.; Derrick, P. J. *Polym. Preprints (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37* (1), 847.

(20) Sanayei, R. A.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1989**, *A26*, 1137.

(21) Suddaby, K. G.; O'Driscoll, K. F.; Rudin, A. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 643.

(22) Enikolopyan, N. S.; Smirnov, B. R.; Ponomarev, G. V.; Belgovskii, I. M. *J. Polym. Sci., Polym Chem. Ed.* **1981**, *19*, 879.

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