Determination of the Mode of Termination in Radical Polymerization via Mass Spectrometry

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Received July 30, 2008; Revised Manuscript Received November 12, 2008

ABSTRACT: We comprehensively explore the use of mass spectrometry (MS) for quantitative determination of the mode of termination, i.e., the extent of disproportionation versus combination, in radical polymerization. Development of the underlying kinetic theory forms a major portion of our endeavors. What emerges from this theory is that the ratio of polymer from disproportionation to combination is a function of chain length and of fundamental kinetic parameters such as the rate of initiation and the rate coefficients for propagation and termination. Therefore, all this information must be at hand in order to determine λ, the fraction of termination by disproportionation. We implement our findings using electrospray−ionization MS results for poly(methyl methacrylate) that we synthesized at 85 °C in benzene employing bis(3,5,5-trimethylhexanoyl) peroxide as initiator, chosen because it has the advantage of yielding only one primary radical species. Our results are well fitted by theory and are found to vary with chain length and initiator concentration as predicted. We also address the issue that signal intensities from macromolecular MS techniques may not give the true molecular weight distribution of a sample because of variation of ionization efficiency with species mass. We devise a way of obtaining λ from data for hypothetical combination and disproportionation species of identical mass. Our final result is $\lambda = 0.63 \pm 0.10$, suggesting that disproportionation is not as rampant in methyl methacrylate systems as commonly thought.

Introduction

One of the first things that one learns about the chemistry of radical polymerization is that termination may occur by both combination and disproportionation,[1] as exemplified in Scheme 1 using methyl methacrylate (MMA). It is remarkable how little is known beyond this. For example, while the mechanism of the combination reaction is straightforward, the site of hydrogen abstraction in the disproportionation reaction is usually only guessed at. This has the consequence that few workers can predict with any confidence what the dominant termination pathway will be for a particular monomer. And where qualitative understanding is lacking, the capacity for quantitative prediction must lie even further away. Making this situation even worse is the lack of secure quantitative information about mode of termination, as illustrated in Figure 1 for MMA. This figure shows literature values[2−15] for λ, the fraction of termination by disproportionation:

$$\lambda = \frac{k_{\mathrm{t,dis}}}{k_{\mathrm{t,dis}} + k_{\mathrm{t,comb}}} = \frac{k_{\mathrm{t,dis}}}{k_{\mathrm{t}}} \tag{1}$$

Here $k_{\mathrm{t,dis}}$ and $k_{\mathrm{t,comb}}$ are the rate coefficients for disproportionation and combination, respectively, as shown in Scheme 1, while k_{t} is the overall rate coefficient for termination. It is evident from Figure 1 that all one can say about the value of λ for MMA is that it is probably closer to 1 (100% disproportionation) than it is to 0 (100% combination) and that it probably increases slightly with temperature, as one would expect.[1] For many other monomers the situation regarding the value of λ is even hazier; in fact, for most monomers there are no literature values of λ available. This emphasizes the urgent need to develop and deploy *reliable*[16,17] methods for determination of λ: this is the subject of this paper.

The situation described above regarding the parameter λ is astonishing for several reasons. First, it is not as if it is an unimportant parameter. For a start, it has a significant effect on molecular weight: in classical kinetics it influences number-average degree of polymerization, $\mathrm{DP_n}$, by a factor of 2 (assuming negligible transfer), as is both well-known and intuitive; this situation has been shown to hold also when termination is chain length dependent.[18] Thus, the mode of termination is important in that it influences polymer properties because these depend intimately on $\mathrm{DP_n}$. Mode of termination plays an additional role in terms of polymer properties in that it determines the end groups that a polymer molecule has (see Scheme 1), something of ever-increasing importance with regard to both material applications and later polymer modification. The second reason why the situation portrayed in Figure 1 is so surprising is because over the past two decades there has been much progress[19] made in accurately measuring other fundamental rate parameters in radical polymerization. Best known in this respect is the use of pulsed-laser polymerization (PLP) in conjunction with size exclusion chromatography (SEC) to determine k_{p}, the rate coefficient for propagation: first proposed in 1987,[20] this method has spawned benchmark k_{p} for styrene,[21] methyl methacrylate,[22] alkyl methacrylates,[23] cyclic methacrylates,[24] butyl acrylate,[25] and, very recently, methacrylic acid.[26] Less appreciated is the associated progress in determining k_{t},[19,27,28] while even transfer rate coefficients may now be more confidently measured.[29,30] And yet when it comes to determination of λ, no robust procedure is acknowledged, let alone is there a recommended one—hence the chaotic situation of Figure 1.

As already mentioned, this is the issue we address in this paper. It was also recently grappled with by Nikitin and Hutchinson,[14] who took to fruition an idea previously sketched out both by Olaj and Schnöll-Bitai[31] and by Sarnecki and Schweer.[32] In simplistic terms, this idea is that the molecular weight distribution (MWD) from a PLP with a high rate of termination will stop at the characteristic chain length in the event of disproportionation and at double this chain length in

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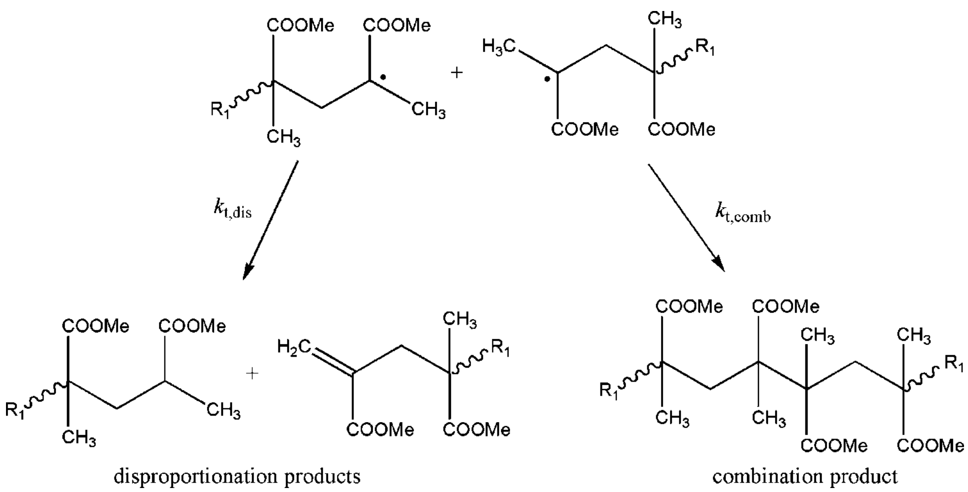
10.1021/ma801732r CCC: $40.75

Scheme 1. Competing Termination Reactions of Disproportionation (Rate Coefficient $k_{t,dis}$) and Combination (Rate Coefficient $k_{t,comb}$) in Radical Polymerization of Methyl Methacrylate[a]



[a] In this work the end group R_1 from initiation is exclusively 2,4,4-trimethylpentyl (see Scheme 2).

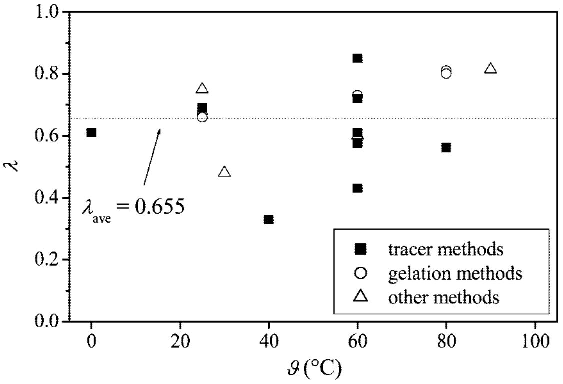
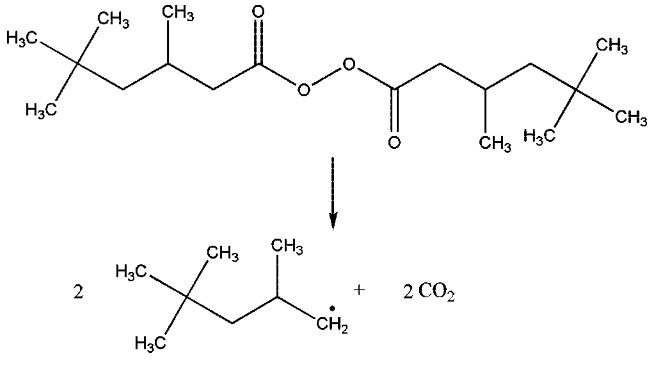


Figure 1. Literature values of λ, the fraction of termination by disproportionation, as a function of temperature for radical polymerization of methyl methacrylate; λ_{ave}, the average of all these values of λ, is also shown. Values were obtained via tracer methods,[2−4] gelation methods,[5−10] and other methods,[11−15] as indicated.

Scheme 2. Overall Decomposition Reaction of Bis(3,5,5-trimethylhexanoyl) Peroxide (BTMHP), the Initiator Used in This Work



the event of combination. Thus, by analyzing the obtained MWD over this range of chain lengths, λ may be determined.[14] While this idea is elegant, there turns out to be a lot of devil in the theoretical detail,[14] and there are restrictive assumptions involved, e.g., no transfer to small molecules and no dead-polymer reactions such as transfer to polymer. Further, accuracy is limited by the fact that the analysis is necessarily of a region of small SEC signal. For these reasons we feel that the scope of this method is limited, and so we pursue a different path for determining λ.

Specifically, in this paper we employ electrospray−ionization mass spectrometry (ESI-MS). In doing so, we build upon work from a decade ago by Zammit et al.,[11,33] who used MALDI (matrix-assisted laser desorption ionization)−MS to estimate λ. The basic idea[33] of this approach is that the resolution of these MS techniques allows separate signals for disproportionation and combination products to be discerned, because the former will have only one end group from the initiator, while the latter will have two (see Scheme 1), and thus they will each have different molar mass. Such resolution of course is not possible with traditional techniques for determining MWD, most notably SEC. It is intuitively obvious that, by quantitative comparison of the signals from disproportionation and combination, it must be possible to obtain λ. What is tremendously appealing about this approach is that it involves direct observation of the products of disproportionation and combination, which is in contrast to the indirect nature of other literature approaches.

What then is new about the present work? (1) From an experimental view, what has changed since the groundbreaking work of Zammit et al.[11,33] is simply that large-molecule MS techniques have improved. Although in this work we use ESI rather than MALDI, this is not intended as a statement that ESI is superior for the purpose at hand. It may be that one method is better suited, and MS experts do indeed debate issues of this nature. However, it seems to us that both can accomplish the job, and which method one uses is primarily a matter of availability. (2) From a theoretical perspective this paper takes the intuitive idea of Zammit et al.[11,33] and gives it a rigorous theoretical footing, showing that analysis to obtain λ is considerably more subtle than previously realized. (3) We devise data analysis procedures that include internal consistency checks and overcome the known limitation of polymer MS techniques not yielding the true MWD.

In this work we build on our recent productive experiences with ESI-MS in applying it to study chain-end characteristics.[34−36] Most importantly for present purposes, these studies showed that, for oligomeric species up to molar mass of about 2000 Da, ESI-MS provides mass peaks that may be unambiguously assigned to disproportionation and combination products, as has also been demonstrated by other workers.[37−39] As monomer we chose to use MMA because much is known about its kinetics (something that will be seen to be important) and because it is well-known to terminate by both disproportionation and combination, making it an ideal candidate for method development. As initiator we chose to use bis(3,5,5-trimethylhexanoyl) peroxide (BTMHP), the decomposition kinetics of which have been comprehensively studied.[40,41] It produces initiating radicals as shown in Scheme 2, which makes clear why BTMHP also is ideal for a study such as this: (1) it is symmetric, and (2) peroxide bond cleavage is followed by near-quantitative decarboxylation.[40] On account of these two characteristics, BTMHP produces only one primary radical species. ESI-MS has indeed confirmed that 2,4,4-trimethylpentyl (TMP) moieties are the only end groups arising from BTMHP.[35] This greatly simplifies interpretation of results because it means there is only one R_1 species in Scheme 1, and thus there are only two types of oligomeric species: those carrying a single TMP end group (there will be pairs of such species separated by 2 Da, see Scheme 1) and those with two TMP end groups.

Experimental Part

Polymerizations. Bis(3,5,5-trimethylhexanoyl) peroxide (BTMHP; AKZO Nobel) and benzene (Merck, 99.7%) were used as received. Methyl methacrylate (MMA; Fluka, 99.0%) was purified via distillation under reduced pressure and thoroughly deoxygenated by purging with nitrogen gas for 10 min. One reaction solution of 0.67 mol L^{-1} MMA in benzene contained 1.6×10^{-2} mol L^{-1} BTMHP and the other 3.3×10^{-2} mol L^{-1}. For the purpose of rate measurement, each reaction solution was divided into multiple samples, all of which were allowed to react in a thermostated block heater at 85 °C. Every 5 min a sample was removed and immediately cooled down in ice water. Then residual solvent and monomer were evaporated off in order to determine the conversion of monomer into polymer by gravimetric analysis. Selected samples of the polymer thus isolated were subjected to MS analysis; only samples from systems with conversion lower than 10% were used for this purpose.

Mass Analysis. The ESI-MS experiments were carried out using a Finnigan LCQ ion-trap mass spectrometer (Thermo Finnigan, San Jose, CA) equipped with an atmospheric pressure ionization source operated in the nebulizer-assisted electrospray mode. Calibration within the mass range 195−1822 Da was carried out with caffeine, MRFA (L-methionylarginylphenylalanylalanine acetate H_2O), and Ultramark 1621 (all from Aldrich). The spectra were obtained in the positive ion mode within the *m/z* range 150−2000 Da at a spray voltage of 4.5 kV and a capillary temperature of 200 °C. Nitrogen was used as sheath gas (flow: 40 units) and He as the bath gas. The polymer samples were dissolved in a 1:3 v/v CH_2Cl_2/methanol mixture at a concentration of about 100 μg mL^{-1}. The samples were introduced into the electrospray interface by injection, via a syringe pump, at 3−5 μL min^{-1} over up to 2 min. Final ESI-MS spectra used in analysis were from coaddition of about 200 individual spectral traces. Reproducibility of the measured *m/z* values was excellent. Relative peak intensities were found to be reproducible within ±5%. A (final) ESI-MS spectrum is shown in Figure 2.

Theoretical Background for Data Analysis

Figure 3 presents a close-up of a portion of the spectrum from Figure 2. The reader is referred to a previous paper of ours for a complete assignment of all signals.[35] At 1099.6 Da there is a calibration peak, but otherwise only two types of signal stand out: MMA oligomers with one 2,4,4-trimethylpentyl (TMP) end group and MMA oligomers with two TMP end groups. Several important conclusions can be drawn from this: (1) For all intents and purposes, BTMHP produced only one primary radical, as expected. (2) Negligible chain transfer occurred; otherwise, oligomers with no TMP end groups would have been observed. (3) Consistent with the findings of many others, both by MS,[11,33,37−39] as here, and by indirect means,[2−10,12−15] combination and disproportionation both occurred to a significant extent.

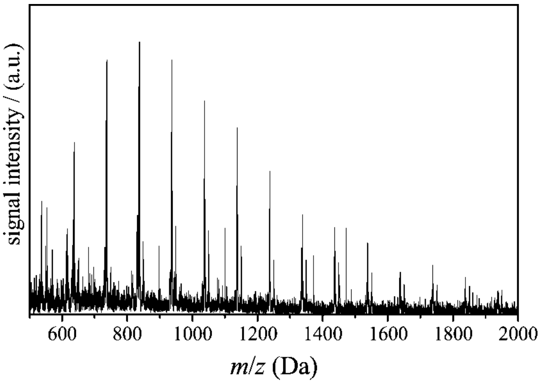


Figure 2. ESI-MS spectrum of poly(methyl methacrylate) obtained from polymerization in benzene solution at 85 °C with 1.6×10^{-2} mol L^{-1} bis(3,5,5-trimethylhexanoyl) peroxide (BTMHP) as initiator. The spectrum is shown over the full mass range used for analysis in this work.

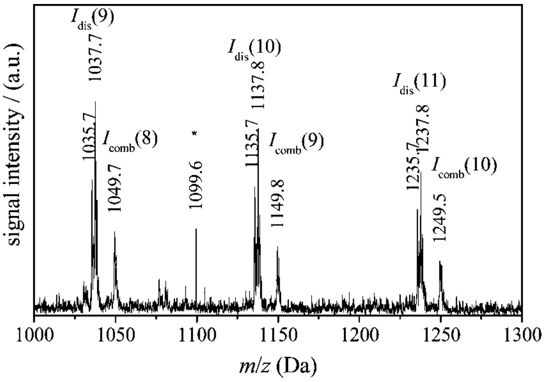


Figure 3. Close-up of Figure 2 over the *m/z* range of 900−1200 Da. The molar mass of each of the prominent peaks is given. All of these peaks are either combination products ("comb"), disproportionation products ("dis"), or internal standard (∗), as indicated. The numbers in parentheses are the number of methyl methacrylate residues. For example, the signals labeled $I_{comb}(8)$ are from oligomer made up of 8 MMA units and 2,4,4-trimethylpentyl at each end.

On the topic of disproportionation, one may wonder why the two members of each pair of disproportionation peaks are of unequal intensity in Figure 3, because Scheme 1 dictates that there should be equal numbers of saturated and unsaturated products from disproportionation. The explanation[34] lies in isotope distributions: the abundance of ^{13}C (∼1%) combined with the large number of carbon atoms in an oligomer means that significant numbers of isotopologues of all oligomers are observed, i.e., molecules containing no ^{13}C atoms, molecules containing 1, containing 2, and so on. This is clearly evident in all oligomer signals in Figure 3. As a consequence of this, at the mass of a saturated disproportionation product with no ^{13}C atoms will also be observed molecules of the corresponding unsaturated product with two ^{13}C atoms. It is this enhancement that is responsible for the asymmetry of disproportionation signals.

Because the disproportionation signals in Figure 3 are of far higher intensity than the combination signals, an immediate conclusion is that disproportionation predominated in this MMA polymerization. Is this correct? And how can one use the information in Figures 2 and 3 to quantitatively determine λ, the fraction of termination by disproportionation? To answer these questions, one needs to understand the factors that determine the *numbers* of molecules of each degree of polymerization that are produced by disproportionation and combination, for this is what gives rise to signal intensities in ESI-MS. These numbers of molecules are determined by the *kinetics* of polymerization, and therefore this topic will now be considered.

Classical Kinetics. We start with—and for the most part we will adhere to—the simplest kinetic scheme for describing radical polymerization, so-called classical kinetics. For continuously initiated polymerizations, as in the present work, one may use steady-state results. For c_{R_i}, the concentration of radicals of chain length i, classical kinetics gives[42]

$$c_{\mathrm{R}_i} = c_{\mathrm{R}_{i-1}}\alpha = c_{\mathrm{R}_0}\alpha^i \tag{2}$$

where α, the probability of propagation, is given by

$$\alpha = \frac{1}{1 + \dfrac{2k_\mathrm{t}c_\mathrm{R}}{k_\mathrm{p}c_\mathrm{M}}} \tag{3}$$

and c_{R_0}, the concentration of primary radicals, is

$$c_{\mathrm{R}_0} = \frac{R_\mathrm{i}}{k_\mathrm{p}c_\mathrm{M}} \tag{4}$$

For chemically initiated polymerization, as here, one has that the rate of initiation is $R_\mathrm{i} = 2fk_\mathrm{d}c_\mathrm{I}$, where f is initiator efficiency, k_d is the rate coefficient for initiator decomposition, and c_I is initiator concentration. Similarly, c_M denotes monomer concentration, while k_p and k_t are the rate coefficients for propagation and termination, respectively. It is evident that the total radical concentration, c_R, is required; the classical, steady-state result for it is

$$c_\mathrm{R} = \left(\frac{R_\mathrm{i}}{2k_\mathrm{t}}\right)^{0.5} \tag{5}$$

It should be clear that k_t has been defined such that the overall rate of termination is $-2k_\mathrm{t}c_\mathrm{R}{}^2$. It is noticeable that transfer has not been included in eqs 3 and 4. This simplification is justified by Figure 3, which, as already explained, indicates that transfer occurred to no detectable extent in our experiments. This is as one would expect for MMA polymerizations with high rate of initiation and no chain transfer agent.

An expression for c_{R_i} is needed because it goes into determining dead-chain concentrations, which are the data yielded by ESI-MS, i.e., the information we seek to understand. The relevant results are

$$\frac{\mathrm{d}c_\mathrm{dis}(i)}{\mathrm{d}t} = 2k_\mathrm{t,dis}c_{\mathrm{R}_i}c_\mathrm{R} = 2\lambda k_\mathrm{t}c_{\mathrm{R}_0}\alpha^i c_\mathrm{R} = \lambda R_\mathrm{i}C\alpha^i \tag{6}$$

$$\frac{\mathrm{d}c_\mathrm{comb}(i)}{\mathrm{d}t} = \sum_{j=1}^{i-1} k_\mathrm{t,comb}c_{\mathrm{R}_j}c_{\mathrm{R}_{i-j}} = (i-1)(1-\lambda)k_\mathrm{t}(c_{\mathrm{R}_0})^2\alpha^i = \frac{1}{2}(i-1)(1-\lambda)R_\mathrm{i}C^2\alpha^i \tag{7}$$

Here $c_\mathrm{dis}(i)$ is the concentration of dead chains of degree of polymerization i yielded by disproportionation, which in the present instance is the concentration of dead chains of length i containing one TMP end group; similarly, $c_\mathrm{comb}(i)$ refers to chains from combination, i.e., containing two TMP end groups. Because of the absence of chain transfer, these are the only two avenues of dead-chain formation that need to be considered. The new parameter in eqs 6 and 7 is the dimensionless quantity

$$C = \frac{2k_\mathrm{t}c_\mathrm{R}}{k_\mathrm{p}c_\mathrm{M}} = \frac{(2k_\mathrm{t}R_\mathrm{i})^{0.5}}{k_\mathrm{p}c_\mathrm{M}} \tag{8}$$

Thus, C is the reciprocal of kinetic chain length; as shown by Olaj et al., it plays a fundamental role in the kinetics of radical polymerization.[18,43] Of course, C is interrelated with rather than separate to α and c_{R_0}, and it need not be included explicitly in equations. Its advantage is that it gives algebraically simplified expressions that enable the true nature of kinetic results to be seen more clearly.

In steady state one has that $\mathrm{d}c_\mathrm{dis}(i)/\mathrm{d}t$ and $\mathrm{d}c_\mathrm{comb}(i)/\mathrm{d}t$ are constant, and thus the values of $c_\mathrm{dis}(i)$ and $c_\mathrm{comb}(i)$ at any given time are related to eqs 6 and 7, respectively, by the same proportionality constant. Similarly, for any given volume of polymer solution one has that $n_\mathrm{dis}(i)$ and $n_\mathrm{comb}(i)$, the number of chains from disproportionation and combination, respectively, are related to $c_\mathrm{dis}(i)$ and $c_\mathrm{comb}(i)$ by the same constant of proportionality. Thus, one may use eqs 6 and 7 to express ratios of $n_\mathrm{dis}(i)$ and $n_\mathrm{comb}(i)$, as for example obtained from ESI-MS. It is such ratios that will be used in this work; hence the need for eqs 6 and 7.

A final point is that the long-chain assumption has not been made in any of the equations of this subsection or the work that follows. First, there is no need for this assumption: all equations are easily derived and used without it. Second, and more crucially, this assumption is best avoided when one is considering oligomers, as in this work.

Zammit et al. Revisited. As just explained, $n \sim \mathrm{d}c/\mathrm{d}t$, from which it follows that

$$\frac{\frac{1}{2}n_\mathrm{dis}(\mathrm{total})}{n_\mathrm{comb}(\mathrm{total})} = \frac{\frac{1}{2}2k_\mathrm{t,dis}(c_\mathrm{R})^2}{k_\mathrm{t,comb}(c_\mathrm{R})^2} = \frac{k_\mathrm{t,dis}}{k_\mathrm{t,comb}} = \delta = \frac{\lambda}{1-\lambda} \tag{9}$$

where $n_\mathrm{dis}(\mathrm{total})$ is the *total* number of chains formed by disproportionation (i.e., summed across all chain lengths) and analogously for $n_\mathrm{comb}(\mathrm{total})$. The above equation also defines the parameter δ and its relationship to $\lambda = \delta/(\delta + 1)$; both parameters are commonly used and are just alternative ways of quantifying the mode of termination.

Equation 9 provides an obvious route to δ (or equivalently λ) from MS data. However, there are two reasons why this approach cannot (yet) be used: (1) The obvious reason is that $n_\mathrm{dis}(\mathrm{total})$ and $n_\mathrm{comb}(\mathrm{total})$ cannot (yet) be obtained because, as Figure 2 makes clear, MS is not (yet) capable of delivering the entire MWD, and thus one cannot sum $n_\mathrm{dis}(i)$ and $n_\mathrm{comb}(i)$ over *all* chain lengths, as is necessary to use eq 9. (2) More subtle but equally important is that MS does not (yet) deliver the true MWD of a polymer because the propensity of molecules to ionize is known to vary with chain length, meaning that the distribution of molecular sizes reaching the MS detector is not the same as the distribution of sizes in the actual polymer sample. While, as indicated, there is optimism that these problems—neither of which are limitations of SEC—may eventually be overcome, for the moment they must be endured.

For the purposes of determining λ, Zammit et al.[11,33] cleverly reasoned that these difficulties may be obviated by considering $n_\mathrm{dis}(i)/n_\mathrm{comb}(i)$ rather than $n_\mathrm{dis}(\mathrm{total})/n_\mathrm{comb}(\mathrm{total})$. It is obvious how this eliminates the first problem above. The second problem is (hopefully) avoided because one is considering molecules of the same chain length and thus (hopefully) of identical tendency to ionize. Therefore, Zammit et al.[11,33] determined $(n_\mathrm{dis}(i)/2)/n_\mathrm{comb}(i)$ from their data and reported these values as δ.

The untested (and unstated) assumption in this procedure is that the relationship in eq 9 holds also for $(n_\mathrm{dis}(i)/2)/n_\mathrm{comb}(i)$. By utilizing the theory of the preceding subsection, we are now in a position to examine this. From eqs 6 and 7 it must be the case that

$$\frac{\frac{1}{2}n_{\mathrm{dis}}(i)}{n_{\mathrm{comb}}(i)} = \frac{1}{(i-1)C\left(\frac{1}{\lambda}-1\right)} = \frac{\delta}{(i-1)C} \tag{10}$$

for steady-state polymerization. It is clear that eq 9 does not hold for $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ in general; in fact, one has that $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i) = \delta$ *only* for $i - 1 = 1/C$, i.e., for $i - 1$ equal to the kinetic chain length (see eq 8). Thus, a more sophisticated data analysis than that of Zammit et al. must be carried out. With this in mind we now investigate the behavior of eq 10.

To begin with, we evaluate eq 10 for different values of c_{I}. Where possible, we have used parameter values appropriate for the conditions of Zammit et al.,[11] who polymerized MMA in toluene at 90 °C with 2,2′-azoisobutyronitrile as initiator. This is to give these calculations some extra context; however, the primary purpose of the calculations is illustrative, so one should not become distracted by the parameter values used—these details are not important. Results are presented in Figure 4 (see the figure caption for parameter values if interested). Two important trends are evident: far from being constant in value, $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ (i) decreases with increasing c_{I} and (ii) decreases with increasing i. In hindsight, the second of these trends is obvious, for it is well-known that the chain length distribution (CLD) from disproportionation is like $\exp(-ki)$ in form, where k is a constant, while that from combination is like $i \exp(-ki)$; thus, the ratio of these two distributions, which is essentially what Zammit et al. determined, must be hyperbolic in form.

In actual fact, Zammit et al. observed both trends i and ii in their data,[11] but lacking any awareness of the underlying theory, they attributed these variations to experimental error. This gives hope that a more enlightened estimate of λ might be rescued from their data. Unfortunately, such a hope is dashed by another trend inherent in eq 10: $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ varies with k_{t}. This is illustrated in Figure 5, which shows that one needs to know the value of k_{t} precisely, not just approximately, in order to extract λ from MS data. The approach that will be used in this work is to measure rate under the same conditions as used to produce polymer for MS analysis. An alternative approach is to measure an average molecular weight, for example, the number-average degree of polymerization, $\mathrm{DP_n}$, which in classical kinetics is given by

$$\mathrm{DP_n} = \left(\frac{1}{C}+1\right)\left(\frac{2}{1+\lambda}\right) \tag{11}$$

This simple equation is more familiar than it might at first look: $1/C$ is kinetic chain length, to which 1 is added to account for initiation (recall: the long-chain approximation is not made here), and this term is then multiplied by a factor accounting for the mode of termination. From eqs 10 and 11 it is clear that given the two pieces of information $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ and $\mathrm{DP_n}$, one can determine the two underpinning parameters λ and C. Assuming that R_{i} and $k_{\mathrm{p}}c_{\mathrm{M}}$ are known, this is equivalent to determining λ and k_{t} (see eq 8). (In all this, be aware that $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ depends only on the coupled parameter C/δ, not on C and δ individually.)

Zammit et al. did not measure rate, and they only carried out SEC analysis of samples made under similar, but not identical, conditions to those of the samples they analyzed by MALDI-MS. Thus, it is not possible to recover a precise estimate of λ from their work. However, their reported value[11] of $\delta \approx 4$ (i.e., $\lambda \approx 0.8$) does seem reasonable to us from our attempts (not presented here) to reprocess their data.

Finally, it is pertinent to mention another source of uncertainty that has lately come to light in regard to the work of Zammit et al. They used time-of-flight (TOF) detection and made the reasonable looking assumption that signal intensity, S, is proportional to number of chains, n.[11] However, Schnöll-Bitai et al. have recently shown that in fact $S \sim n(m) \times m^{0.5}$ for TOF detection, where m is molar mass;[44,45] further, they have illustrated that this result has a significant transforming effect in converting S into n.[45] Because Zammit et al. only took the ratio of S values for signals of similar m (see above), one may anticipate that the "Schnöll−Bitai transformation" would only have had a small quantitative effect on their results because the two values of $m^{0.5}$ would have been similar for most ratios. However, properly this transformation should be carried out, and we note that its effect will be greatest at small chain lengths, where relative m differences will be greater.

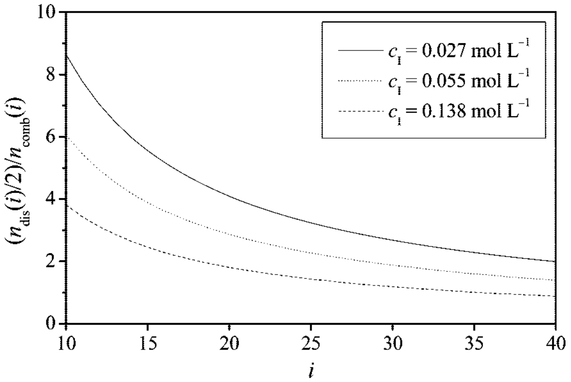


Figure 4. Variation of $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ with chain length i, as calculated using eq 10 with parameter values appropriate for AIBN-initiated polymerization of MMA in toluene at 90 °C, the experimental conditions of Zammit et al.:[11] $\lambda = 0.8$, $c_{\mathrm{M}} = 0.909$ mol L^{-1}, $fk_{\mathrm{d}} = 5.36 \times 10^{-4}$ s^{-1}, $k_{\mathrm{p}} = 1\,630$ L mol^{-1} s^{-1},[22] and the three indicated initiator concentrations. For the only unknown parameter was used $k_{\mathrm{t}} = 1 \times 10^{8}$ L mol^{-1} s^{-1}.

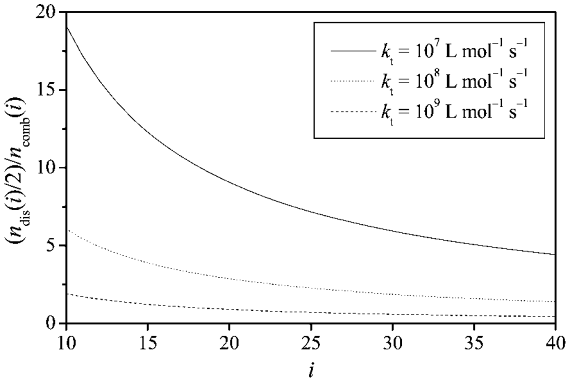


Figure 5. Effect of k_{t} on the variation of $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$ with chain length i, as calculated using eq 10. Parameter values are as in Figure 4, except for $c_{\mathrm{I}} = 0.055$ mol L^{-1} at all times and k_{t} varied as indicated.

The Approach of This Work. Once one comprehends that eq 9 does not hold for individual i, it follows that one must not be wedded to the ratio $(n_{\mathrm{dis}}(i)/2)/n_{\mathrm{comb}}(i)$, for it has no immediate mechanistic significance (see eq 10). In this work we have preferred to use the *fraction* of chains of length i formed by disproportionation, $F_{\mathrm{dis}}(i)$, which is

$$F_{\mathrm{dis}}(i) = \frac{n_{\mathrm{dis}}(i)}{n_{\mathrm{dis}}(i) + n_{\mathrm{comb}}(i)} \tag{12}$$

There is no reason why one must use this ratio, but we find it convenient because it is restricted to the interval from 0 to 1 and it gives an immediate feeling for the extent of disproportionation at a particular chain length.

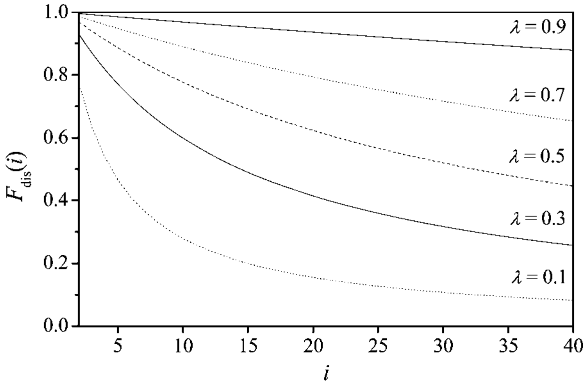


Figure 6. Variation with i of $F_{\mathrm{dis}}(i)$, the fraction of chains of length i formed by disproportionation, as calculated using eq 13 with $C = 6.4 \times 10^{-2}$ (in line with the experiments of this work) and varying λ as indicated.

From eqs 6, 7, and 12 one obtains that

$$F_{\mathrm{dis}}(i) = \frac{1}{1 + \frac{1}{2}(i-1)C\left(\frac{1}{\lambda} - 1\right)} = \frac{1}{1 + \frac{1}{2}(i-1)C\left(\frac{1}{\delta}\right)} \tag{13}$$

Although this is not the same as eq 10, it still gives the same qualitative behavior seen in Figures 4 and 5; i.e., $F_{\mathrm{dis}}(i)$ decreasing with increasing i, increasing c_{I} and increasing k_{t}. Thus, the understanding gained from the preceding subsection of work carries over. To give a feeling for the behavior of eq 13, in Figure 6 we show evaluations of it for varying λ and constant C, now using a value in line with the experiments of this work (see parameter values given at the beginning of the following section), as opposed to those of Zammit et al.[11] in our previous calculations. It is evident that over the i accessed by ESI-MS in this work (see Figures 2 and 3) $F_{\mathrm{dis}}(i)$ is sensitive to the value of λ. This finding is significant in that it theoretically validates the method of using MS to determine λ.

In this work our approach in essence is to determine $F_{\mathrm{dis}}(i)$ from MS spectra and then use eq 13 to analyze these values in order to obtain λ.

Chain-Length-Dependent Reactivities. The defining assumption of classical kinetics is that of chain-length-independent reactivities. With time it has become clear that this assumption is nonphysical for both propagation and termination: for MMA it is now widely accepted that propagation rate coefficients decrease in value by a factor of ~10 over the first few chain lengths before reaching a constant value,[46] while termination rate coefficients keep decreasing over all chain lengths.[27,28] The important question arises as to whether these complicating factors undermine the theory presented above and thus render it invalid for data analysis. This will now be investigated.

We consider chain-length-dependent termination (CLDT) because it is the principal phenomenon that gives rise to nonclassical behavior.[47] Instead of eqs 4 and 2 respectively one has[42,47,48]

$$c_{\mathrm{R}_1} = \frac{R_{\mathrm{I}}}{k_{\mathrm{p}}c_{\mathrm{M}} + 2\sum_{j=1}^{\infty} k_{\mathrm{t}}^{1,j} c_{\mathrm{R}_j}} \tag{14}$$

$$c_{\mathrm{R}_i} = \frac{k_{\mathrm{p}}c_{\mathrm{M}}c_{\mathrm{R}_{i-1}}}{k_{\mathrm{p}}c_{\mathrm{M}} + 2\sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j} c_{\mathrm{R}_j}}, \quad i = 2, \infty \tag{15}$$

while instead of eqs 6 and 7 respectively one has

$$\frac{\mathrm{d}c_{\mathrm{dis}}(i)}{\mathrm{d}t} = 2\lambda c_{\mathrm{R}_i} \sum_{j=1}^{\infty} k_{\mathrm{t}}^{i,j} c_{\mathrm{R}_j}, \quad i = 1, \infty \tag{16}$$

$$\frac{\mathrm{d}c_{\mathrm{comb}}(i)}{\mathrm{d}t} = (1-\lambda) \sum_{j=1}^{i-1} k_{\mathrm{t}}^{j,i-j} c_{\mathrm{R}_j} c_{\mathrm{R}_{i-j}}, \quad i = 2, \infty \tag{17}$$

The only new parameter in these equations is $k_{\mathrm{t}}^{i,j}$, the rate coefficient for termination between two radicals of chain lengths i and j. Clearly this one change has a greatly complicating effect, and it results in no simple expression for $F_{\mathrm{dis}}(i)$ being available (cf. eq 13). In general, what must be done is to solve eqs 14 and 15 iteratively to obtain all c_{R_i} and then use these values in eqs 16 and 17. The reader is referred elsewhere for more complete details.[42,49,50]

With any complex model, just as vital an issue as the model itself is the use of physically correct parameter values in it. Recent experiments have confirmed the so-called "composite model" for termination,[51] finding that[52−55]

$$k_{\mathrm{t}}^{i,i} = k_{\mathrm{t}}^{1,1} i^{-0.63}, \quad i \leq 100$$

$$k_{\mathrm{t}}^{i,i} = k_{\mathrm{t}}^{1,1} (100)^{-0.63+0.16} i^{-0.16}, \quad i > 100 \tag{18}$$

for *n*-alkyl methacrylates, including MMA, at low conversions, as in the experiments of this work. Therefore, we used eq 18 (and the geometric-mean model for cross-termination[51]) in simulations with eqs 13−17. A set of results for $F_{\mathrm{dis}}(i)$ over a range of i that is relevant to this work is shown in Figure 7; similarly, parameter values appropriate for the polymerizations of this work (see the following section) have been used in calculations. Also presented in Figure 7 are values from eq 13 with identical parameter values. For the calculations with CLDT, the value of $k_{\mathrm{t}}^{1,1}$, the rate coefficient for termination between monomeric radicals, was chosen so as to give the same chain-length-averaged termination rate coefficient, $\langle k_{\mathrm{t}} \rangle$, as the value of k_{t} used in eq 13. Of course, $\langle k_{\mathrm{t}} \rangle$ is evaluated as follows:

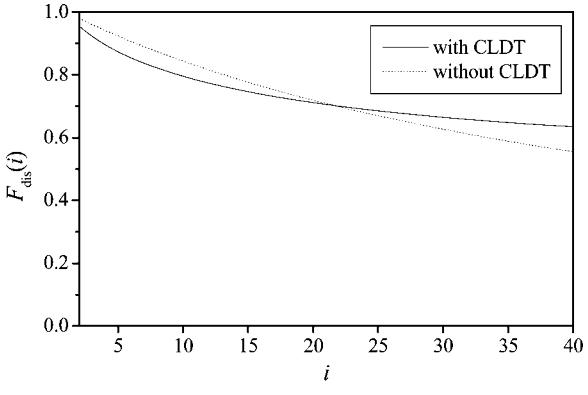


Figure 7. Effect of chain-length-dependent termination (CLDT) on the variation with i of $F_{\mathrm{dis}}(i)$. Unbroken line ("with CLDT"): eqs 14–18 with $k_{\mathrm{t}}^{1,1} = 8 \times 10^8$ L mol^{-1} s^{-1}; dotted line ("without CLDT"): eq 13 with $k_{\mathrm{t}} = 2.3 \times 10^8$ L mol^{-1} s^{-1}. Parameter values common to both sets of calculations: $2fk_{\mathrm{d}}c_{\mathrm{I}} = 1.9 \times 10^{-5}$ mol L^{-1} s^{-1}, $c_{\mathrm{M}} = 0.66$ mol L^{-1}, $k_{\mathrm{p}} = 1.47 \times 10^3$ L mol^{-1} s^{-1}, and $\lambda = 0.7$ (all as in the high-c_{I} experiment of this work).

$$\langle k_t \rangle = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_t^{i,j} \frac{c_{R_i} c_{R_j}}{{c_R}^2} \tag{19}$$

Figure 5 shows why it is necessary to have $\langle k_t \rangle = k_t$ in comparing results: so that differences in $F_{dis}(i)$ cannot be attributed to differences in the overall rate of termination.

While Figure 7 shows that CLDT does have an effect on $F_{dis}(i)$, it also shows that the effect is not great. In hindsight, this is not surprising: while CLDT does alter the shape of the radical and dead-chain CLDs, remember that our interest here is in $n_{dis}(i)/n_{comb}(i)$, so one can expect cancelation of the effects of CLDT to a large extent. Figure 7 provides proof that this is the case. Certainly the differences in Figure 7 are small compared to those in Figure 6. This means that in modeling $F_{dis}(i)$ data the value of λ will have a far greater effect than the nature of the termination model used, a matter still of some uncertainty. This both argues for and legitimizes the use of eq 13 to analyze MS data, even though the underlying assumption of chain-length-independent termination is incorrect. In fact, as part of this work we did use eqs 14−18 to model our MS data (using the global fitting approach of the following section), always finding that variation of parameters in eq 18 had only a minor effect on the best-fit value of λ (±0.05 at most);[56] for this reason we do not present these results in this publication.

We also carried out sample calculations employing a recent model for chain-length-dependent propagation (CLDP) that has been found to describe MMA data.[46,57] This revealed more complicated behavior than with CLDT alone, no doubt related to the fact that introducing CLDP increases $\langle k_p \rangle$, the chain-length-averaged propagation rate coefficient, *and* decreases $\langle k_t \rangle$,[46,58] both of which effects generally act to increase $F_{dis}(i)$ (see eqs 8 and 13 and Figure 5). Without a more thorough theoretical investigation, not to mention greater certainty about the extent to which small-chain k_p values are elevated, it does not seem justified to draw conclusions about how CLDP affects the variation of $F_{dis}(i)$ with i for real systems. However, what can reasonably be concluded is that CLDP should only possibly have a significant effect on $F_{dis}(i)$ values for the i over which CLDP is operative, i.e., for very small i, say $i \leq 8$.[46] Therefore, in our data analysis we will be careful not to place any undue weight on such data.

In summary, the important finding of this subsection is that, all else being equal, a physically reasonable CLDT model gives $F_{dis}(i)$ values that are not significantly different to those of eq 13, and therefore this equation may be used to analyze MS data even though the underpinning assumption of chain-length-independent reactivities is flawed. Of course, if there were certain knowledge about the nature of CLDT and CLDP, then one would be compelled to analyze data using this information. But in the absence of such certainty it seems fully justified to use the classical model given that we have shown that it does not introduce any significant error in the present utilization. Besides, simplicity can be a virtue.

Results and Discussion

Rate Parameters. The work of the previous section shows that one needs to know the values of other kinetic parameters in order to analyze MS data to obtain λ. The values we used are as follows. From the literature we have that $k_p = 1468$ L mol^{-1} s^{-1} for MMA at 85 °C[22] and that[56,59] $f = 0.53$ and[60] $k_d = 5.44 \times 10^{-4}$ s^{-1} for BTMHP in benzene at the same temperature. Values of c_M and c_I have already been given in the Experimental Part. This leaves only k_t. Because it is a parameter whose value depends on so many variables,[27] it was necessary to determine it for the specific reaction conditions used to make our samples for MS analysis. Thus, we measured conversion as a function of time for our precise polymerization conditions and then determined k_t from these measurements using[28]

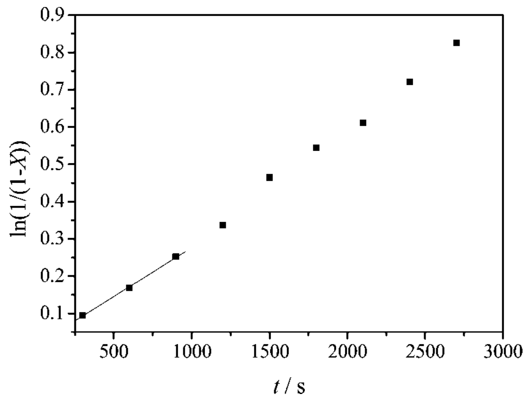


Figure 8. −ln(1 − X), where X is fractional conversion, as a function of time, t, for polymerization of methyl methacrylate in benzene solution at 85 °C with 3.3 × 10^{-2} mol L^{-1} bis(3,5,5-trimethylhexanoyl) peroxide (BTMHP) as initiator. Points: experiment; (straight) line: fit to low-conversion data (used to obtain k_t, see text).

$$\frac{-\mathrm{d}[\ln(1 - X)]}{\mathrm{d}t} = k_p \left(\frac{f k_d c_I}{k_t} \right)^{0.5} \tag{20}$$

Here X is the fractional conversion of monomer into polymer. Figure 8 presents −ln(1 − X) vs t from our experiment with higher initiator concentration. To obtain k_t, we used the slope of the low-conversion portion of this data (see the linear fit in Figure 8) in eq 20; this is because our MS analyses were only of polymer made under low-conversion conditions (see Experimental Part). This procedure yielded $k_t = 1.41 \times 10^8$ L mol^{-1} s^{-1}, a value of expected magnitude for an MMA polymerization carried out at high temperature and with high rate of initiation. Therefore, it is the value we henceforth use in data analysis.

Relative Populations. As has been seen, data analysis to obtain λ requires the relative populations of polymerization products. Properly obtaining these from an MS spectrum raises several subtle issues. The first is that, as already explained, each chemical species actually gives rise to a cluster of peaks, where each peak is for a particular isotopologue. Thus, one must determine the area of each peak and then sum all the areas in an isotopic cluster in order to obtain the relative number of molecules of a particular species. We denote this sum of integrals $I_{dis}(i)$ and $I_{comb}(i)$ for species produced by disproportionation and combination, respectively. Because $n \sim I$, one has that

$$F_{dis}(i) = \frac{I_{dis}(i)}{I_{dis}(i) + I_{comb}(i)} \tag{21}$$

This is the exact way to determine $F_{dis}(i)$ from MS data, and it is what we used at the outset of this study.

A difficulty with this procedure is that signal intensities decrease as m/z increases. This is evident in the results of Figure 2; eqs 6 and 7 make clear why this is the case. The effect of this is that the signal-to-noise ratio is poorer at higher m/z, which makes it difficult to determine all peak areas. We found that a way to overcome this difficulty was to use only the first peak in an isotopic distribution, i.e., the peak from species without any ^{13}C atoms. Because such a species must have a relatively high abundance, its MS peak will have a superior signal-to-noise ratio. A subtlety here is that, as explained earlier, the peaks for a disproportionation oligomer actually consist of two overlapping sets of peaks: one for the unsaturated species and the other for its saturated analogue (see Scheme 1). However, the very first peak of such a cluster arises only from unsaturated oligomer with no ^{13}C atoms, and so it contains no overlapping contributions to resolve. Thus, its area may be compared with that of the first peak of a cluster arising from combination in order to obtain the relative number of each species, i.e., unsaturated disproportionation product and combination product. Of course, for every unsaturated disproportionation product there is also (exactly) one saturated disproportionation product, so by doubling the area of the first disproportionation peak one obtains an index of the total number of disproportionation products in a cluster.

Even for the first peak of a cluster it can be impossible to precisely determine the area at high *m*/*z*, such is the noise in the lower portions of the peak. However, there is significantly less noise in peak height, and therefore a further refinement in our approach was the standard one of using peak height rather than area. Overall, then, one has

$$F_{\mathrm{dis}}(i) = \frac{2h_{\mathrm{dis}}(i)}{2h_{\mathrm{dis}}(i) + h_{\mathrm{comb}}(i)} \tag{22}$$

where h denotes the height of the first peak in a cluster (cf. the use of I in eq 21 to denote the area of a set of peaks). Of course, we carried out benchmarking, using peaks with good signal-to-noise to evaluate $F_{\mathrm{dis}}(i)$ via both eq 21 and eq 22. There was excellent agreement, thereby justifying the method of eq 22, which is both easier to use and, as explained, able to be implemented more widely. Therefore, it is this method that we have used for the results we present in what follows.

Lastly, an assumption in the above procedure is that signal intensity is proportional to number of molecules. As discussed earlier, this is not the case for TOF detection.[44,45] However, to the best of our knowledge this assumption is appropriate for an ion-trap analyzer, as was used by us. Further, even if this assumption turns out to be flawed, the procedure of only taking the ratio of heights of peaks of similar m will largely eliminate any error, as already explained in the context of Zammit et al.'s work.

Global Modeling. It is manifest that our experimental results for $F_{\mathrm{dis}}(i)$, which are the points in Figure 9, show the trends expected from the theory of the preceding section: most importantly, $F_{\mathrm{dis}}(i)$ decreases with increasing i rather than being constant in value, while it is also evident that $F_{\mathrm{dis}}(i)$ is higher for the lower initiator concentration, as anticipated from Figure 4.

Given these encouraging signs, naturally we were motivated to obtain the value of λ from our data. The most obvious way to do this is to fit our data to eq 13. This is a two-parameter equation. However, we know the value of C (eq 8) for our experiments—an important point to note is that it varies with c_{I}—and so λ is the only unknown. Thus, one has the simple task of one-parameter fitting. Results of this process are also presented in Figure 9. It is evident that eq 13 with $\lambda = 0.63$ gives an acceptable fit to all our data. As is shown, this process suggests an uncertainty of approximately ±0.07 in this fitted value of λ. Importantly, there is random scatter in the fitting residuals, which gives confidence in both the model of eq 13 and the way in which we extract $F_{\mathrm{dis}}(i)$ from our raw MS data. Arguably even more important is that both data sets are consistent with the same value of λ, which is as expected because the balance between disproportionation and combination should not be altered by c_{I}.

Pointwise Modeling. While the global modeling approach of Figure 9 may overall be termed a success, there were several ways in which we were motivated to achieve better: (1) Rather than varying λ and trying to judge how well the data was fitted by the resulting predictions of eq 13, we wondered whether the data itself could directly yield the value of λ. (2) So as to facilitate comparison, we desired a clear way of presenting fitting results from our two data sets (lower and higher c_{I}) *on the one plot* (because $F_{\mathrm{dis}}(i)$ varies with c_{I}, it is difficult to overlay the two parts of Figure 9 meaningfully). (3) Rather than fitting yielding residuals of $\Delta F_{\mathrm{dis}}(i)$, we sought a procedure that delivered residuals $\Delta\lambda$.

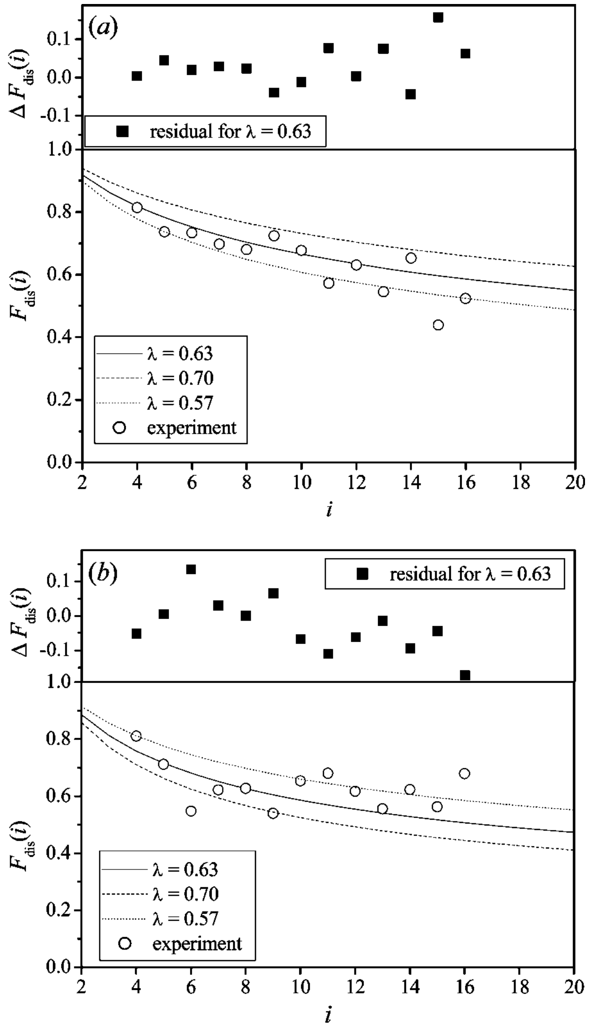


Figure 9. Bottom panels: $F_{\mathrm{dis}}(i)$, the fraction of chains formed by disproportionation, as a function of chain length, i, where the points are experimental values (obtained from our MS data using eq 22) and the curves are evaluations of eq 13 with the indicated values of λ. Top panels: $\Delta F_{\mathrm{dis}}(i)$, the difference between eq 13 with $\lambda = 0.63$ (middle curves of the bottom panels) and experimental values of $F_{\mathrm{dis}}(i)$. (a) (top figure): results from using BTMHP concentration $c_{\mathrm{I}} = 1.6 \times 10^{-2}$ mol L^{-1}; (b) (bottom figure): results from $c_{\mathrm{I}} = 3.3 \times 10^{-2}$ mol L^{-1}.

All the above objectives can be met by the following pointwise modeling procedure. Equation 13 can be rearranged to give

$$\delta = \frac{(i-1)CF_{\mathrm{dis}}(i)}{2(1 - F_{\mathrm{dis}}(i))} \tag{23}$$

This equation may not be used for $i = 1$, for which $F_{\mathrm{dis}}(i) = 1$ regardless of the value of λ. But for all other $F_{\mathrm{dis}}(i)$ one may use eq 23 to determine δ and hence $\lambda = \delta/(\delta + 1)$. This means that from every data point a value of λ may be obtained.

Results from using this procedure with our data are presented in Figure 10. Addressing the issues raised above: (1) As shown,

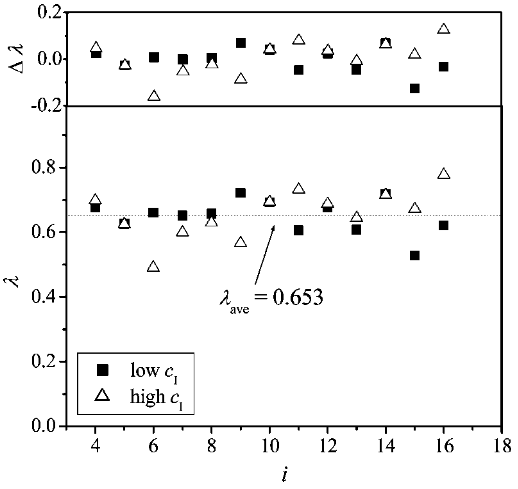


Figure 10. Bottom panel: fraction of termination by disproportionation, λ, as a function of chain length, i, as obtained using eq 23 with each experimental $F_{dis}(i)$ value of Figure 9; λ_{ave}, the average of all the thus obtained values of λ, is indicated. Top panel: all values of $\Delta\lambda = \lambda - \lambda_{ave}$. Filled squares ("low c_I"): results from using BTMHP concentration $c_I = 1.6 \times 10^{-2}$ mol L^{-1}; empty triangles ("high c_I"): results from $c_I = 3.3 \times 10^{-2}$ mol L^{-1}.

the data yields an average value $\lambda = 0.65$ in a way that is free of any bias. (2) Results for each data set may now be directly compared, and it is indisputably clear that we see no variation of λ with c_I, exactly as should be the case. Pleasing for the same reason is the absence of any systematic variation of λ with i. (3) From the residuals, $\Delta\lambda$, one may easily estimate an uncertainty of approximately ±0.10 in our average value of λ.

While global modeling has its uses—for example, one can visually appraise the quality of a fit—for the given reasons we recommend the pointwise method of this subsection for obtaining best estimates of λ. Further, because the pointwise method clearly reveals the lack of any systematic dependence of λ on c_I or i, we believe it establishes the quality of our data and the rectitude of our model.

Toward Ultimate Accuracy. Soft MS techniques are already revolutionizing macromolecular science through the precise species identification that they enable. However, there is still skepticism about the capacity of these techniques to deliver MWDs, and it is not recommended that they be used in this regard. The problem is that the propensity of molecules to ionize is known to vary with mass and with chemical composition, meaning that the MS detector does not deliver the true MWD of a sample. In the future this may be overcome through the coupling of MS and SEC,[61] but for now it is a problem that must be lived with. It is an issue for our method of λ determination because it relies not just on identification of species but also on accurate measurement of their population. Borrowing from Zammit et al.,[11,33] we have therefore used *only* relative populations $n_{comb}(i)/n_{dis}(i)$ in our data analysis (see eq 12), the idea being that even if there is systematic error in these individual populations, it should be very similar in each—because species of identical degree of polymerization are involved—and should therefore largely cancel out in taking the ratio. The results of Figure 10 strongly endorse this thinking. However, one might still be concerned about the possibility of error, and so we were inspired to do better.

Specifically, Schemes 1 and 2 and Figure 3 reveal that the ratio $n_{comb}(i)/n_{dis}(i)$ actually involves species that differ in mass by 113 Da on average, this arising from the extra TMP end group that a combination product bears. So if there is any mass dependence of ionization probability, then values of $n_{comb}(i)/n_{dis}(i)$ returned by MS will not be the true values for a sample. The way to eliminate any such bias is to compare signals of combination and disproportionation species of identical mass. Of course, such species do not exist, and nor would it help if they did, for then one would not be able to distinguish the two types of species by MS, this ability being a cornerstone of our method. However, it is possible to use species that are very nearly identical in mass: a combination product of degree of polymerization $i - 1$ will have mass just 12 Da more than a saturated disproportionation product of degree of polymerization i and 14 Da more than the analogous unsaturated product, i.e., a difference of $\Delta(m/z) = 13$ Da on average.

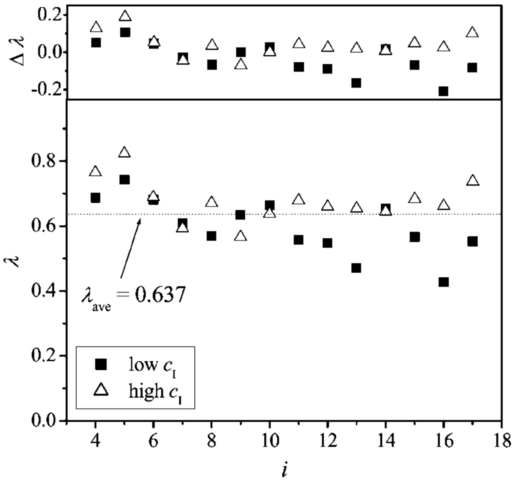


Figure 11. As for Figure 10, except that λ has been obtained using $F_{dis}(i,i-1)$ values in eq 26 (see text).

We chose to exploit this by defining

$$F_{dis}(i, i-1) = \frac{n_{dis}(i)}{n_{dis}(i) + n_{comb}(i-1)} \tag{24}$$

As explained, this ratio involves species with nearly identical mass, and so one can have confidence that it eliminates as completely as possible any effects of variation of ionization tendency with mass. Using eqs 6 and 7, one may show that classical kinetics predicts that

$$F_{dis}(i, i-1) = \frac{1}{1 + \frac{1}{2}(i-2)C\left(\frac{1}{\delta}\right)\left(\frac{1}{\alpha}\right)} \tag{25}$$

With our pointwise modeling approach in mind, one may rearrange this equation to obtain

$$\delta = \frac{(i-2)C\alpha^{-1}F_{dis}(i, i-1)}{2(1 - F_{dis}(i, i-1))} \tag{26}$$

This equation may only be used for $i > 2$ because $F_{dis}(2,1) = 1$ always. Also note that $\alpha = 1/(1 + C)$ (see eqs 3 and 8) is known if C is known, as is the case here.

Repeating the procedure of the preceding subsection, we have evaluated $F_{dis}(i,i-1)$ values from our MS spectra and then used eq 26 to determine λ from every such data point. Results are presented in Figure 11. The consistency checks of having λ independent of c_I and i are still met. Although the average value of $\lambda = 0.637$ is different to that from $F_{dis}(i)$ values ($\lambda = 0.653$, see Figure 10), this difference is miniscule and is well within scatter. Indeed, the similarity of these values could also be regarded as another (and major) consistency check fulfilled. Thus, one must conclude that the approach of using $F_{dis}(i)$ values to determine λ is validated. This is not to say that our MS delivered the true MWD of the sample; rather, it is just to say

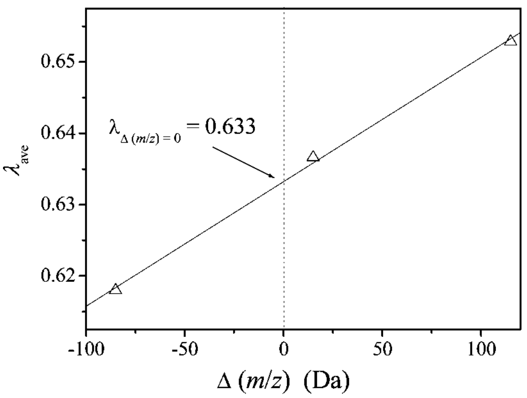


Figure 12. Points: average λ values, λ_{ave}, from pointwise modeling (as in Figures 10 and 11) as a function of $\Delta(m/z)$, the average mass/charge difference of the MS signals used to obtain each λ_{ave} value (see text); unbroken line: best fit to the points; interpolation: value of the best fit for $\Delta(m/z) = 0$ (see text).

that any errors do indeed largely cancel out in taking the ratio $n_{comb}(i)/n_{dis}(i)$.

In the analysis we have just carried out there is nothing constraining one to use disproportionation and combination signals with a difference in degree of polymerization of 1. This opens up the possibility of using, for example, combination signals in tandem with disproportionation signals that are degree of polymerization 2 more. This is of interest because such combination signals are the ones *immediately less* than disproportionation signals in mass, by 87 Da on average, as opposed to $F_{dis}(i,i-1)$ involving combination signals immediately *more* in mass (see Figure 3). In other words, one would still be using signals that are very close together in mass. Running with this idea, one defines and has that

$$F_{dis}(i, i-2) = \frac{n_{dis}(i)}{n_{dis}(i) + n_{comb}(i-2)} = \frac{1}{1 + \frac{1}{2}(i-3)C\left(\frac{1}{\delta}\right)\alpha^{-2}} \quad (27)$$

which leads to

$$\delta = \frac{(i-3)C\alpha^{-2}F_{dis}(i, i-2)}{2(1 - F_{dis}(i, i-2))} \quad (28)$$

We used eq 28 and the definition of eq 27 to analyze our data again in the pointwise fashion, obtaining a plot extremely similar to Figures 10 and 11 in appearance and with the slightly lower average value of $\lambda = 0.618$.[56] This engenders still further confidence in our methodology.

The real purpose we had in mind in using $F_{dis}(i,i-2)$ values is that this analysis enables the following creative exercise to be carried out. It was mentioned before that ideally one would like to compare combination and disproportionation signals of identical mass in order to eliminate completely any effects of MS ionization tendency on mass. An additional advantage of such a comparison is that it should eradicate any error due to signal intensity having an unsuspected dependence on m (as discussed earlier in relation to TOF detection, where there is a known dependence on $m^{44,45}$). With λ now having been obtained using $F_{dis}(i)$, $F_{dis}(i,i-1)$, and $F_{dis}(i,i-2)$ values, these involving average differences $\Delta(m/z)$ of 113, 13, and −87 Da, respectively, in peak mass, one can plot the obtained average λ as a function of $\Delta(m/z)$ and interpolate to $\Delta(m/z) = 0$. This has been done in Figure 12. The point of so doing is that the resulting value of λ pertains to hypothetical combination and disproportionation species of identical mass, i.e., species for which there is no mass-related ionization bias in MS. Thus, we regard the value of $\lambda = 0.633$ obtained by this interpolation procedure (see Figure 12) as being the best possible estimate of λ from our data. It is worth noting that this best estimate is identical to that from our initial modeling procedure, the simple global fitting of eq 13 to our data ($\lambda = 0.63$, Figure 9). This suggests that we have established that the simple procedure is sufficient to obtain reliable values of λ.

With reference to the value $\lambda = 0.633$, of course we are not claiming that this work has delivered λ that is accurate to three decimal places: the $\Delta\lambda$ values in Figures 10 and 11 make clear that this is not the case, and on the basis of these values together with the procedure carried out above, one would say that $\lambda = 0.63 \pm 0.10$ is the conclusion from our data. The important points here are that we have striven to eliminate all possible sources of systematic error and that our efforts to do so in this subsection have resulted only in minor changes to λ, suggesting that there was relatively little such error in the first place.

This is not to say that we have eliminated every possible source of error. For example, while we have devised here a way of overcoming the effect of any mass-related variation of MS ionization rates, our procedure does not eliminate end-group effects: it is possible that combination and disproportionation species of identical mass may have different ionization probabilities due to having different end groups, i.e., 2 and 1 TMP groups, respectively (see Schemes 1 and 2). Of course, it is not possible to eradicate any such error completely because utilizing this end-group difference is the founding principle of our method. Besides, it is hard to imagine that an additional nonpolar TMP group could have anything but a very minor influence on ionization efficiency. Further, if there were such an effect, then it would become more pronounced at very low i. However, our results show no sign at all of any such systematic error that diminishes with chain length (see Figures 10 and 11).

Conclusion

Our value of $\lambda = 0.63 \pm 0.10$ at 85 °C nestles well among the literature values of Figure 1,[56] which have mean value $\lambda = 0.655$, as shown. In particular, we are encouraged by how close our value is to the value $\lambda = 0.75 \pm 0.04$ recently obtained by Nikitin and Hutchinson[14] using a method very different from ours (see the Introduction). This said, their value was obtained at 25 °C. So the implication of these two values is that the fraction of disproportionation decreases with increasing temperature. This is opposite to expectation.[1] In view of this situation, we tender four concluding comments.

(1) The first is a reminder that history proves—see Figure 1!—that λ is a very difficult parameter to measure accurately. This needs to be remembered in appraising (new) methods and results: one should be more tolerant of apparent shortcomings than one is with other rate parameters.

(2) In determining λ, appearances can be deceptive. The dominance of the disproportionation signals in Figures 2 and 3 gives the initial (and commonly believed) impression that termination is predominantly by disproportionation. Thus, it comes as something of a surprise that a proper kinetic analysis finds that this data is best described by $\lambda = 0.63$, which betokens a relatively even balance rather than disproportionation being overwhelming. One therefore wonders if some of the literature values of λ, many of which are a little higher than ours (see Figure 1), might have been obtained more through qualitative impression than rigorous kinetic analysis.

(3) The MS-based method for determining λ involves indisputable identification of the species from combination and disproportionation. We feel this is a crucial advantage over other methods, all of which are indirect and do not involve unambigu-

ous separation of the two types of species. Thus, one must assume one has the ideally desired behavior (see discussion in the Introduction), whereas with MS one can be certain of what one is seeing. For example, in this work we know with certainty that transfer was not undermining our method. Of course, we do not pretend that MS is as strong in delivering populations as it is in identifying species—it is not, and this is an issue for our method. However, we believe we have devised an analysis approach that fully overcomes this shortcoming. For this reason we have every confidence in the value of λ we have obtained, and we fully recommend our method, especially in view of the certainty that macromolecular MS techniques will continue to improve.

(4) More experiments need to be done! It may be that λ actually decreases with temperature for MMA. This will only be established by deploying our method to measure λ as a function of temperature, for both MMA and other monomers. It is high time that our near complete ignorance about the mode of termination in radical polymerization came to an end.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft for the project Bu 426/10 is gratefully acknowledged. The authors thank Dr. Holm Frauendorf for kindly performing the mass spectrometric analyses. We are indebted to Dr. Greg Smith for his assistance in carrying out calculations. M.B. is grateful to the University of Canterbury for the Visiting Erskine Fellowship that helped bring this work to completion. P.V. acknowledges receipt of a Heisenberg-Professorship (DFG). G.T.R. acknowledges Prof. Tom Davis for starting him on the path of this work.

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MA801732R