Chain Length Dependence of Radical−Radical Termination in Free Radical Polymerization: A Pulsed Laser Photolysis Investigation

Devon A. Shipp[†] **and David H. Solomon***

Polymer Science Group, Department of Chemical Engineering, The University of Melbourne, Victoria 3010, Australia

Trevor A. Smith

Photophysics Laboratory, School of Chemistry, The University of Melbourne, Victoria 3010, Australia

Graeme Moad*

CSIRO Molecular Science, Bag 10, Clayton South 3169, Victoria, Australia

Received June 24, 2002; Revised Manuscript Received December 9, 2002

ABSTRACT: A new method for analyzing the chain length dependence of termination rate coefficients ($k_t(i,j)$ where i and j are the chain lengths of the reacting radicals) in low conversion free radical polymerizations is described. The method involves comparing experimental molecular weight distributions of polymers formed in pulsed laser photolysis experiments with those predicted by kinetic simulation. The method is enabled by direct measurements of the concentration of radicals generated per laser pulse. Knowledge of the radical concentrations should mean that the only unknowns in the simulations are the termination rate coefficients. The analysis demonstrates the need for chain length dependent termination rate constants in describing polymerization kinetics. Polymerization kinetics were analyzed in terms of two models which purport to describe the functional form of $k_t(i,j)$. Use of a Smoluchowski model for $k_t(i,j)$, in conjunction with independently measured monomer diffusion coefficients, provides molecular weight distributions that closely match those obtained experimentally. However, the finding that reasonable fits can also be obtained using a geometric mean model to describe $k_t(i,j)$ indicates molecular weight distributions alone do not contain sufficient information for unambiguous model discrimination.

Introduction

Free radical polymerization comprises three main processes: initiation, propagation, and termination.[1] Of these, termination, the cessation of growth of propagating radicals, is the most difficult to study because it involves a number of mechanisms, all of which may operate simultaneously during the polymerization. The dominant termination process in polymerizations of most common monomers in the absence of added transfer agents or inhibitors is by radical−radical reaction (also called bimolecular termination).[1] This process has proved the most resistant to in-depth study, and the detailed mechanism has been and remains the subject of much controversy.

Perusal of the literature (as summarized in the *Polymer Handbook*[2,3]) reveals a marked lack of agreement in reported termination rate coefficients (k_t) for polymerizations of even the most common monomers. A major contributing factor to this situation is the fact that bimolecular termination of radicals is a diffusion-controlled process. This means that the termination rate coefficient should be sensitive to the size of the reacting species and to various factors that affect the viscosity (or microviscosity) of the reaction medium. Such factors include the monomer conversion, the molecular weight (chain length) of any polymer present, solvent quality, etc. It follows that if the termination rate is dependent on the chain lengths of the reacting species, then the values of k_t quoted in the literature should be considered a weighted average of the individual rate constants, $k_t(i,j)$, where i and j are the chain lengths of the radicals.[4,5] Analysis of the situation is rendered complex by the fact that, at any given instant during the polymerization, a wide range of molecular sizes is simultaneously present. It also follows that the overall or average k_t obtained under a given set of polymerization conditions cannot necessarily be translated to other conditions since the molecular weight distribution of the propagating species and the various experimental parameters mentioned above are different.

While the probable chain length dependence of the termination process has been recognized since the late 1950s,[4−8] it remains a standard practice to utilize a single chain length independent termination rate coefficient ($\langle k_t \rangle$) in kinetic analysis of free radical polymerization. This can be attributed to several factors: (a) use of a single $\langle k_t \rangle$ is often sufficient to describe the kinetics of conventional polymerization processes (under a given set of conditions); (b) difficulties in obtaining reliable and unambiguous experimental values for individual $k_t(i,j)$; (c) lack of agreement on how to describe the functional form of the chain length dependence of $k_t(i,j)$. Russell et al.[9,10] and de Kock et al.[11,12] have discussed the “termination problem” in detail.

The PLP−MWD technique has become the standard method for determining propagation rate constants (k_p) in free radical polymerizations.[13−17] This method involves analyzing the molecular weight distribution (MWD) of polymers formed in pulsed laser photolysis (PLP) experiments. It has been found that the propagation rate constant can be evaluated using the expression

---

[†] Current address: Department of Chemistry, Clarkson University, Potsdam, NY 13699-5810.

10.1021/ma0209951 CCC: $25.00

$$\frac{\upsilon_\mathrm{p}^n}{n} = k_\mathrm{p}[\mathrm{M}]t_\mathrm{f} \tag{1}$$

where υ_p^n is the length of the polymer chain formed during a period of n laser pulses and corresponds to the inflection point on the low molecular weight side of the nth peak in the MWD, [M] is the monomer concentration, and t_f is the time between the laser pulses. Kinetic simulations[13,18−23] have provided theoretical justification for the method and, in particular, the use of inflection points (as determined from maxima in the first derivative of the MWD) to measure υ_p^n. These theoretical studies[18,21,23] also show how the overall *shape* of the MWD (in particular, the height and breadth of the peaks that make up the MWD) is governed by the concentration of propagating radicals, which is, in turn, determined by the concentration of primary radicals generated per laser pulse ($[\mathrm{I}^\bullet]_0$) and the termination rate coefficients. It was, therefore, proposed[18] that measurements of $[\mathrm{I}^\bullet]_0$ should enable a more reliable estimation of k_t and potentially the values of $k_\mathrm{t}(i,j)$.

We have recently described[24] a novel method of determining $[\mathrm{I}^\bullet]_0$ in PLP experiments and, in a preliminary communication,[22] have shown how this knowledge can be applied to estimate $\langle k_\mathrm{t}\rangle$ for styrene polymerization. In this paper, we provide more detail of this analysis and examine the functional form of the chain length dependent termination rate coefficient, $k_\mathrm{t}(i,j)$, for low conversion polymerizations. Two systems have been examined: the homopolymerizations of styrene and methyl methacrylate in benzene solution.

Experimental Section

Monomers, styrene (Aldrich), and methyl methacrylate (MMA) (Fissons) were purified by passage through a column of basic alumina and vacuum distillation. Benzene (AR grade, BDH) was refluxed over sodium under nitrogen and distilled. Azobis(methyl isobutyrate) (AIBMe) was obtained from Wako (Japan) and used without further purification.

The required mass of monomer was placed into a 5 mL volumetric flask. The appropriate volume of an initiator stock solution (~0.01 M in benzene) was added and the volume made up to the mark with benzene. Approximately 1.5 mL of this solution was then placed into a degassing bulb attached to a quartz cuvette. The solution was degassed with at least four freeze−evacuate−thaw cycles (~10^{-7} Torr), transferred to the cuvette under vacuum, and sealed. The cuvette was placed in a thermostated sample holder.

A frequency-tripled Continuum Nd:YAG laser (355 nm) was used as the laser source, and each experiment consisted of 250 laser pulses at 30 mJ/pulse and repetition rates corresponding to $t_\mathrm{f} = 0.1$ or 0.2 s. After polymerization, the excess monomer and solvent were removed under vacuum (<25 °C). The conversion of monomer to polymer was determined gravimetrically to be <1%.

The MWDs were determined on a Waters gel permeation chromatograph (GPC) consisting of a 510 pump, a U6K injector, three GPC columns (Styragel HR-1, HR-4, and 10^5 Å), and a 410 RI detector. Tetrahydrofuran was used as the mobile phase eluting at 1.0 mL min^{-1}. The temperature of the columns was maintained at 30 °C. The system was calibrated with narrow molecular weight standards of either polystyrene (seven standards, molecular weight range 2630−355 000; TOSOH Corp., Japan) or PMMA (five standards, molecular weight range 3400−265 000; Polymer Laboratories, U.K.). All calibrations were linear fits with correlation coefficients > 0.9995.

After converting elution volumes to molecular weights via the calibration curve, chain lengths were obtained by dividing the molecular weight of the polymer by the molecular weight of the monomer. After baseline subtraction, the $w(\log i)$ MWD was generated by normalizing the peak maximum to 1. The derivative ($\mathrm{d}w(\log i)/\mathrm{d}(\log i)$) of the $w(\log i)$ MWD was obtained using the “Derivative” macro in the Kaleidagraph program on an Apple Macintosh computer.

Table 1. Calculated $[\mathrm{I}^\bullet]_0^\mathrm{av}$ Values from Eq 2 Using a Given $[\mathrm{AIBMe}]_0$ and $[\mathrm{I}^\bullet]_0$, with $f = 0.5$ and $N = 250$

$[\mathrm{AIBMe}]_0$ ($\times 10^{-3}$ M)	$[\mathrm{I}^\bullet]_0$ ($\times 10^{-6}$ M)	$[\mathrm{I}^\bullet]_0^\mathrm{av}$ ($\times 10^{-6}$ M)
2.00	3.10	2.57
0.999	1.52	1.26
0.365	0.51	0.43

The computer simulations were carried out on either a Cray YMP-4E or Cray J90 computer, with a program written in Fortran 77. The simulations used numerical integration[18] to solve the complete set of differential equations that result from analysis of a polymerization scheme encompassing the following reactions:

initiation: $\mathrm{I}^\bullet + \mathrm{M} \rightarrow \mathrm{P}_1^\bullet \quad k_i$

propagation: $\mathrm{P}_i^\bullet + \mathrm{M} \rightarrow \mathrm{P}_{i+1}^\bullet \quad k_\mathrm{p}(i)$

termination

combination: $\mathrm{P}_i^\bullet + \mathrm{P}_j^\bullet \rightarrow \mathrm{P}_{i+j} \quad k_\mathrm{tc}(i,j)$

disproportionation: $\mathrm{P}_i^\bullet + \mathrm{P}_j^\bullet \rightarrow \mathrm{P}_i + \mathrm{P}_j \quad k_\mathrm{td}(i,j)$

where $k_\mathrm{t}(i,j) = k_\mathrm{tc}(i,j) + k_\mathrm{td}(i,j)$.

All chains up to a predefined limit (300 units) are considered discretely. Longer chains are not neglected but are effectively considered as a composite species that equates to the partial zeroth moment of the molecular weight distribution.[25] Thus, their contributions to the molecular weight distribution are fully accounted for without the need for any approximations.

Values of $[\mathrm{I}^\bullet]_0$ were determined as described in our previous paper.[24] This involved conducting a similar PLP experiment in the presence of a nitroxide bearing a fluorophore and measuring the changes in nitroxide concentration during the course of the experiment. For the present work, it has also been necessary to allow for the fact that the concentration of initiator, and therefore $[\mathrm{I}^\bullet]_0$, decreases slightly during the course of the experiment. Since $[\mathrm{I}^\bullet]_0$ is proportional to the initiator concentration,[24] an average $[\mathrm{I}^\bullet]_0$ (designated $[\mathrm{I}^\bullet]_0^\mathrm{av}$) was calculated using eq 2.

$$[\mathrm{I}^\bullet]_0^\mathrm{t} = \sum_{p=1}^{N}\left\{\left([\mathrm{I}_2]_0 - 2f\sum_{s=1}^{p-1}[\mathrm{I}^\bullet]_0^\mathrm{s}\right)\left(\frac{[\mathrm{I}^\bullet]_0}{[\mathrm{I}_2]_0}\right)\right\} \tag{2a}$$

and

$$[\mathrm{I}^\bullet]_0^\mathrm{av} = \frac{[\mathrm{I}^\bullet]_0^\mathrm{t}}{N} \tag{2b}$$

where $[\mathrm{I}^\bullet]_0^\mathrm{t}$ is the total primary radical concentration, $[\mathrm{I}_2]_0$ the initial initiator concentration, f the initiator efficiency, $[\mathrm{I}^\bullet]_0^\mathrm{s}$ the primary radical concentration generated at pulse number s, N the total number of pulses in a PLP−MWD experiment, and $[\mathrm{I}^\bullet]_0$ the primary radical concentration generated by the first laser pulse. The values of $[\mathrm{I}^\bullet]_0$ and $[\mathrm{I}^\bullet]_0^\mathrm{av}$ under the various experimental conditions used are presented in Table 1.

Results and Discussion

The problem of how the termination rate coefficient varies with chain length has proved exceedingly difficult and is still a matter of controversy. A common approach is to scale k_t according to some type of power law, an approach based on theory[26−32] and/or experimental

Table 2. Experimental Data for PLP−MWD Experiments of Styrene (Entries 1−4; [Styrene] = 4.40 M) and MMA (Entries 5−10; [MMA] = 2.20 M) at 25 °C (All Have a Total of 250 Pulses and Laser Energy = 30 mJ/pulse)

entry	t_f (s)	[AIBMe] ($\times 10^{-3}$ M)	$[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ ($\times 10^{-6}$ M)	υ_p^1	υ_p^2	k_p^1 (L mol^{-1} s^{-1})	k_p^2 (L mol^{-1} s^{-1})
1	0.1	0.999	1.26	35.7	70.4	81.1	80.0
2	0.1	0.366	0.43	36.1	69.1	82.0	78.5
3	0.2	0.999	1.26	69.5	130.0	79.0	73.9
4	0.2	0.366	0.43	74.2	142.6	84.3	81.0
5	0.1	2.00	2.57	67.6	131.6	307.3	299.1
6	0.1	0.999	1.26	68.5	133.1	311.4	302.5
7	0.1	0.366	0.43	70.6	136.2	320.9	309.5
8	0.2	2.00	2.57	130.0	258.7	295.5	294.0
9	0.2	0.999	1.26	137.9	276.6	312.7	295.9
10	0.2	0.366	0.43	140.3	272.9	318.9	310.1

data.[33−42] Such studies indicate that (for a constant polymer volume fraction) the chain length dependence of $k_t(i,j)$ can be described by

$$k_t(i,j) \sim N^{-\gamma}$$

where N represents an average of i and j, the length of the two reacting chains. The value of the exponent γ depends on polymer concentration regime (dilute, semidilute, or melt) and the chain lengths (entangled or not) such that γ is <1 for shorter, more mobile chains (at very low, or “zero”, conversions, γ has been predicted[30] to be $\sim$0.16) and $\gamma > 1$ for longer, entangled, chains.

The Smoluchowski diffusion model[43] and the geometric mean model[33−39] are two widely used models for describing the functional form of the chain length dependence of $k_t(i,j)$. The Smoluchowski model has as its origin the proposal that termination rates are governed by simple center-of-mass diffusion and has been applied to small radical termination kinetics.[27,44] The geometric mean and related models are largely empirical in origin but have been justified with the claim that they better represent segmental diffusion processes, as required to bring the chain ends together which is assumed to be the rate-determining step.

According to the Smoluchowski model, values of $k_t(i,j)$ depend on the translational diffusion coefficients of the reacting radical chains as shown in eq 3.

$$k_t(i,j) = 2\pi(D_i + D_j)\sigma N_A \tag{3}$$

where D_i is the translational diffusion coefficient for a chain of length i, σ is the capture radius, and N_A is Avogadro’s number.

Russell et al.[10,45,46] have proposed the following expressions (4a−4c) for D_i

$$i < X_c: \quad D_i = (D_{\mathrm{mon}})/(i^a) \tag{4a}$$

$$i > X_c: \quad D_i = (D_{\mathrm{mon}})(X_c^{\,b-a})/(i^b) \tag{4b}$$

$$i > z: \quad D_i = 0 \tag{4c}$$

where D_{mon} is the diffusion coefficient of the corresponding monomer, X_c is a critical chain length distinguishing “short” chains from “long” chains, a and b are exponents controlling the degree of the chain length dependence, and z is a truncation chain length.

According to the geometric mean model, $k_t(i,j)$ is described by eq 5[33−39]

$$k_t(i,j) = k_{t0}(ij)^{-\alpha} \tag{5}$$

where k_{t0} is the termination rate coefficient for a reaction between two chains of unit length each (i.e., $k_t(1,1)$), i and j are the chain lengths of the radical species, and α is the exponent controlling the degree of the chain length dependence.

A complicating factor in choosing a model for $k_t(i,j)$ is that the radical chain lengths are often wildly different. In the PLP experiments in the period immediately after the laser pulse, at least one of the reacting chains will be very short (<15 units[18]) and even in the dark period will be much shorter on average than in polymerizations with conventional (steady-state) initiation. In these circumstances, use of equations based on Rouse diffusivity[26−32] or models that have been specifically derived to describe polymer kinetics and dynamics of entangled melts is unnecessary or inappropriate. Very short chains whose dynamics are likely to control the rate of termination are better treated as small molecules.[27] Furthermore, Rouse dynamics evolve into the Smoluchowski model under such conditions.[32] For these reasons we have not attempted to use these models and restrict our discussion to the Smoluchowski model (which has been successfully used to model diffusion of small molecules or radicals[27,44]) and the widely used (albeit physically unrealistic) geometric mean model.

Experimental PLP−MWD Data. A series of PLP−MWD experiments were performed for both styrene and MMA solutions at 25 °C, with a variety of average primary radical concentrations $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ and two values of t_f (0.1 and 0.2 s). The different $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ values were obtained by changing the initial initiator concentrations $[\mathrm{AIBMe}]_0$. Table 2 summarizes the conditions (e.g., monomer, $[\mathrm{AIBMe}]_0$, $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$, t_f) and the chain lengths at the points of inflection (from both the first and second peaks in the MWD, υ_p^1 and υ_p^2, respectively) and k_p values derived from the MWDs.

The MWDs for two samples of polystyrene formed in similar PLP experiments (same initiator/monomer concentration and laser pulse energy) are shown in Figure 1 and serve to illustrate the reproducibility of the PLP−MWD method as applied in the present work. The k_p values (obtained by analysis of these MWDs using the standard PLP−MWD equation[14,16]) are the same within experimental error (81 and 82 L mol^{-1} s^{-1}) and in excellent agreement with previous work and the IUPAC benchmark value at 25 °C (84 L mol^{-1} s^{-1}).[15] More importantly, the overall shape and the position and relative heights of the first and subsequent peaks in the MWD are very similar. A further indication of the quality of the data is the good agreement between the k_p values derived from the first and second points of inflection.

We previously reported that existing experimental data for styrene polymerization were consistent with k_p values being chain length dependent for the first few

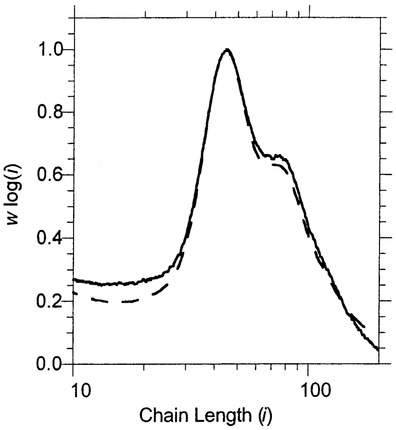

Figure 1. Comparison of two MWDs of polystyrene formed in duplicate PLP experiments (as in entry 2, Table 2).

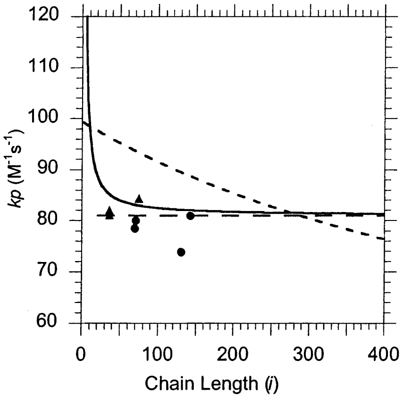

Figure 2. Comparison of experimental k_p for styrene polymerization (data from first point of inflection, ▲; data from second point of inflection, ●) with the IUPAC benchmark value[16] (— — —) and predictions assuming a chain length dependent k_p of the form described by Deady et al.[18] (—) and Olaj et al.[63] (- - -) (eq 6a in ref 63 with $k_p(0) = 94.4$ M^{-1} s^{-1}, $A = 64.3$, $B = 711.6$).

propagation steps.[18] The work of Fischer and Radom[47] and Gridnev and Ittel[48] provides experimental support for there being some chain length dependence of k_p over the first few propagation steps in MMA polymerization. The chain length dependence is thought to have its origin in the different conformational and steric environment of short chain propagating species and is predicted by theoretical calculations. Olaj et al.[49] have recently reported that k_p values for styrene and MMA polymerization obtained from PLP−MWD experiments appear to show a significant chain length dependence over a larger range of chain lengths (<1000 units). The effect, which may be in addition to that mentioned above, is attributed to variations in the local monomer concentration in the immediate region of the chain end. In Figures 2 and 3 we compare our experimental data with the IUPAC benchmark value[15] and predictions based on a chain length dependent k_p.[18] While the experimental scatter is too large to say whether there is chain length dependence of the form discussed in our earlier paper, the data appear inconsistent with the form of chain length dependence suggested by Olaj et al.[49] In the following discussion, it has been assumed that k_p is independent of chain length (see also later discussion).

Some of the apparent scatter seen in Figures 2 and 3 reflects a trend for k_p to decrease slightly with increasing $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ (also see Table 2). This is observed in both the styrene and MMA k_p values but is most pronounced for MMA and is independent of t_f. Such systematic trends have been observed by others but in most cases are masked by experimental error (often as much as 10%). Such trends are predicted by simulation.[18,21,23] It is noteworthy that Beuermann[23] has recently examined changes in measured k_p with chain length (effected by changes in t_f) and $[\mathrm{I}^\bullet]_0$ using computer simulations and concluded that measured k_p values may vary up to 30% from the input value for k_p. These simulation results qualitatively agree with our experimental findings with regard to the dependence of υ_p^1 (and hence k_p) on t_f and $[\mathrm{I}^\bullet]_0$.

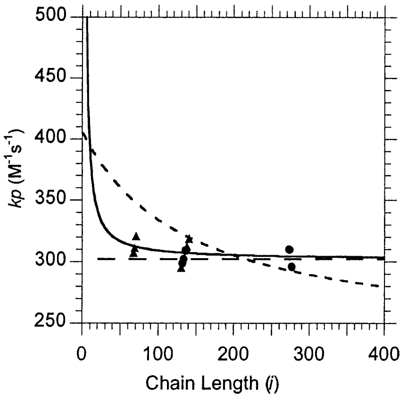

Figure 3. Comparison of experimental k_p for MMA polymerization (data from first point of inflection, ▲; data from second point of inflection, ●) with the IUPAC benchmark value[16] (— — —) and predictions assuming a chain length dependent k_p of the form described by Deady et al.[18] (—) and Olaj et al.[63] (- - -) (eq 6a in ref 63 with $k_p(0) = 406.6$ M^{-1} s^{-1}, $A = 169.0$, $B = 135.4$).

Table 3. Parameter Values for the Smoluchowksi[9,10] and Geometric Mean[36] Models of $k_t(i,j)$ for Styrene and MMA

		monomer	
model	parameter	styrene	MMA
Smoluchowski	σ (Å)	3	3
	D_{mon} (m^2 s^{-1})	1.5×10^{-9}	1.5×10^{-9} or 1.3×10^{-9}
	a	0.5	0.5
	b	0.6	0.6
	X_c	86	78
geometric mean	k_{t0} (M^{-1} s^{-1})	1.97×10^8	1.22×10^8
	α	0.16	0.075 or 0.15

Table 4. Parameter Values for PLP−MWD Simulations[15,16]

parameter	styrene	MMA
k_i (L mol^{-1} s^{-1})	3000	3000
k_p(L mol^{-1} s^{-1})	84	323
[monomer] (M)	4.40	2.20
% combination	85	60
no. of pulses	10	10

Values of $k_t(i,j)$ in Styrene Polymerization. Simulations of the PLP−MWDs were performed using the model and algorithm outlined by Deady et al.[18] The values of the various parameters required to apply the Smoluchowski and geometric mean models are listed in Table 3. The parameters for the Smoluchowski model come from Russell,[9,10] and the geometric mean model is from Mahabadi.[36] Table 4 gives the other relevant parameters for the simulations. To reproduce the experimentally determined $w(\log i)$ MWD (i.e., the calibrated GPC chromatogram) more fully, the simulated MWD data were subjected to a Gaussian broadening

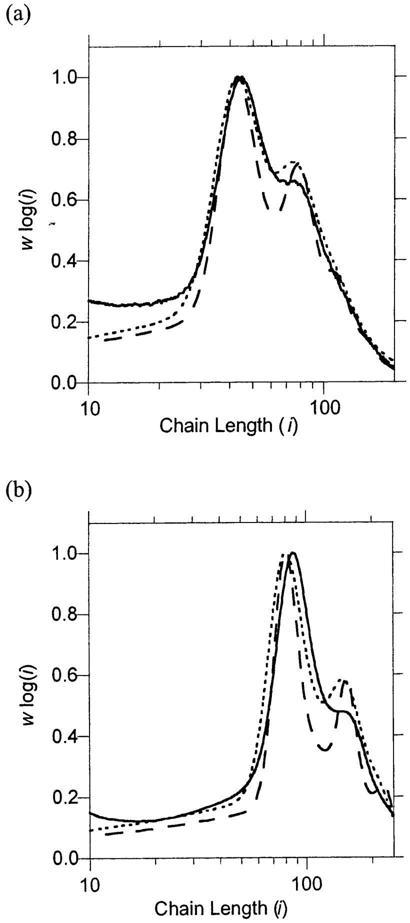

Figure 4. Comparison of experimental (—) and simulated MWDs (unbroadened, - - -; broadened, • • •) for styrene PLP with $[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 4.3 \times 10^{-7}$ M and $k_t(i,j)$ described by the Smoluchowski equation. (a) Table 2, entry 2 ($t_f = 0.1$ s); (b) Table 2, entry 4 ($t_f = 0.2$ s). Simulations: $k_t(i,j)$ given by eqs 3 and 4 with parameters given in Table 3; other simulation parameters as given in Table 4.

function to account for axial dispersion in the GPC analysis. The method of Buback et al.[21] was used with $\sigma_v b = 0.05$ (σ_v is a dispersion parameter, and b is the slope of the calibration curve), which was estimated for the GPC apparatus used in this study and is typical for optimized systems.[21]

The experimental, as well as the unbroadened and broadened simulated, MWDs of PLP-generated polystyrene (entries 1−4 in Table 2) are shown in Figures 4 and 5. These show that for both t_f times, and both $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ conditions, the broadened simulated MWDs closely approximate the experimental MWDs. It is of interest to note that the line broadening leaves the relative heights of consecutive peaks in the MWD unchanged. Such a comparison of relative peak heights for consecutive peaks between unbroadened simulated and experimental MWD's was used in this work to provide a preliminary assessment of goodness of fit. These results indicate that $k_t(i,j)$ obtained using the Smoluchowski model, in conjunction with independently determined monomer diffusion coefficients, can provide an adequate description of the MWD.

Using similar data to those shown in Table 3 for the Smoluchowski model, Russell[9] has calculated that $\langle k_t \rangle$ for a conventional MMA polymerization is 1.91×10^8 L mol^{-1} s^{-1}. This value is much higher than what had been observed experimentally (values are typically in the range $(1-3) \times 10^7$ L mol^{-1} s^{-1}).[40] To explain the differences between the calculated and experimental values of $\langle k_t \rangle$, Russell[9] suggested a number of possible additions to the basic center-of-mass diffusion model for $k_t(i,j)$. These were (i) that a spin probability factor (p_s) be introduced into the Smoluchowski equation, (ii) making long chain−long chain termination impossible, (iii) introducing an extra term to account for different diffusion characteristics of the radical chains following encounter of the radical pair (i.e., diffusion behavior of a chain is different when in close vicinity of another chain), and (iv) allowing for the possibility that some $k_t(i,j)$ values be chemically controlled.

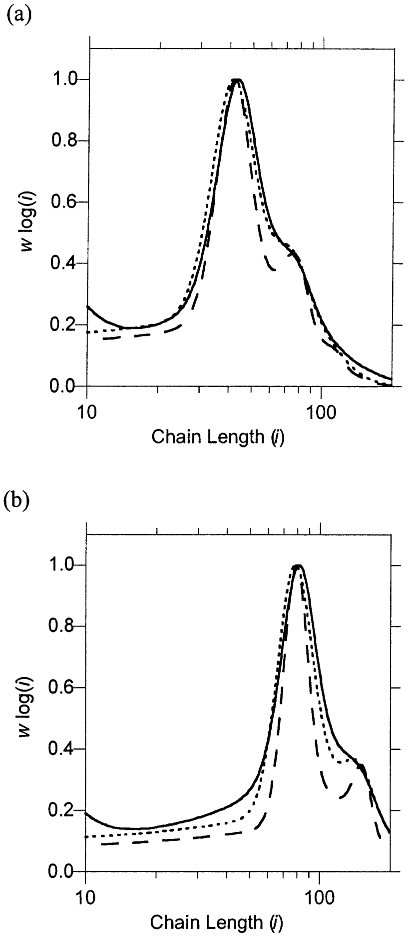

Figure 5. Comparison of experimental (—) and simulated MWDs (unbroadened, - - -; broadened, • • •) for styrene PLP with $[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 1.26 \times 10^{-6}$ M and $k_t(i,j)$ described by the Smoluchowski equation. (a) Table 2, entry 1 ($t_f = 0.1$ s); (b) Table 2, entry 3 ($t_f = 0.2$ s). Simulations: $k_t(i,j)$ given by eqs 3 and 4 with parameters given in Table 3; other simulation parameters as given in Table 4.

While none of these, or indeed, other possibilities were rejected, the spin probability factor was a favored explanation.[9] In view of this, it seems worthwhile to consider the effect of introducing a spin probability factor into the Smoluchowski equation in the present work.[9,46,50] In such a case eq 3 becomes

$$k_t(i,j) = 2\pi p_s(D_i + D_j)\sigma N_A \qquad (6)$$

where $0.25 \le p_s \le 1.0$.

This spin probability factor is rationalized in terms of a termination reaction being "spin allowed" only when the radical pair is in a singlet spin state. Thus, assuming a random distribution of spin states, it is possible

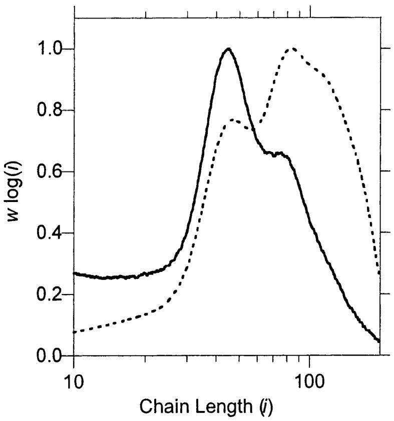

Figure 6. Comparison of experimental (—) and simulated MWDs (broadened, • • •) for styrene PLP with $[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 4.3 \times 10^{-7}$ M and $k_t(i,j)$ described by the Smoluchowski equation incorporating a spin probability factor $p_s = 0.25$. Experiment from Table 2, entry 2 ($t_f = 0.1$ s). Other simulation parameters as given in Table 4.

that only one in four radical−radical encounters actually results in a reaction.[50] If, on the other hand, the rate of spin flipping is fast, with respect to the radical chain diffusion, then p_s may equal 1.

While $p_s = 0.25$ may hold for small molecule reactions in the liquid phase, it is questionable that this would be appropriate for macromolecular species, where diffusion takes place on much slower time scales, thereby increasing the chance of spin-flipping (and hence reaction) to occur. Certainly at high viscosities this would be the case and is also likely at the low conversions and viscosities of interest here. This means that p_s is also a chain length dependent parameter.

For the simulations presented in Figures 4 and 5 it is assumed that $p_s = 1$. Figure 6 shows that introducing a $p_s = 0.25$ (with other parameters the same) results in very poor correlation between the simulated and experimental MWDs. A value of $p_s = 0.25$ also suggests a value of $k_t(1,1)$ of 8.5×10^7 L mol^{-1} s^{-1}. This value is inconsistent with reported rates of the (self-) termination rate coefficients of small radicals (generally 5×10^8−5×10^9 L mol^{-1} s^{-1}).[51] With $p_s = 1$ the calculated value for $k_t(1,1)$ is 3.4×10^8 L mol^{-1} s^{-1}.

The finding that the Smoluchowski equation provides a satisfactory description of the experimental MWD does not mean that it is the correct model. It is also important to test other models to see whether they also provide an adequate description. The geometric mean model of $k_t(i,j)$ (eq 3) has been considered in this light.

Mahabadi[36] examined the polymerization of styrene at 30 °C (bulk, initiated by AIBN, spatially intermittent polymerization method) and obtained the following values for k_{t0} and α:

$$k_{t0} = 1.97 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1};\quad \alpha = 0.12$$

A simulation using these parameters was performed, and the resulting MWD was compared with an experimental MWD. These data are shown in Figures 7 and 8 (simulations have added Gaussian broadening). Agreement between the simulated and experimental MWD becomes worse for long chain lengths, suggesting that the degree of chain length dependence of $k_t(i,j)$ is underestimated. Use of a larger α leads to an overestimation of the second overtone peak but gives a better approximation for longer chain lengths (also shown in Figures 7 and 8 with $\alpha = 0.16$). In recent work, Olaj et al. (e.g., ref 52) have used $\alpha = 0.16$ within the geometric mean model.

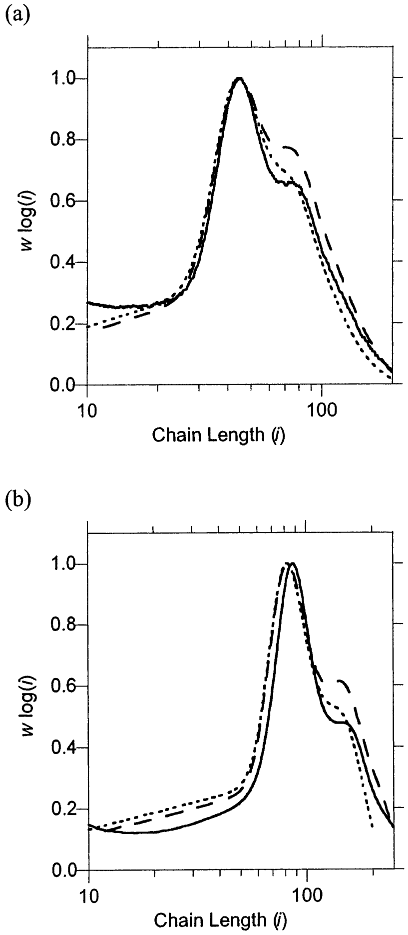

Figure 7. Comparison of experimental (—) and simulated MWDs for styrene PLP with $[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 4.3 \times 10^{-7}$ M and $k_t(i,j)$ described by the geometric mean model ($\alpha = 0.12$, • • •; $\alpha = 0.16$, - - -). (a) Table 2, entry 2 ($t_f = 0.1$ s); (b) Table 2, entry 4 ($t_f = 0.2$ s). Simulations: $k_t(i,j)$ given by eq 5 and parameters given in Table 3; other simulation parameters as given in Table 4.

These data indicate that the geometric mean model can also provide a reasonable description of $k_t(i,j)$ for the experimental data, although the fits are generally not quite as good as was found with the Smoluchowski model. The geometric mean model seems to provide a better fit to those MWDs where a larger, rather than smaller, $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ was used (compare Figure 8 with Figure 7). This may reflect some systematic error. Given that the Smoluchowski model performs well under both $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ data sets and that the experimentally determined $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ can be treated with confidence,[24] it appears that the geometric mean model is less appropriate for describing $k_t(i,j)$ in styrene polymerization under our experimental conditions.

Values of $k_t(i,j)$ in Methyl Methacrylate Polymerization. The analysis of $k_t(i,j)$ in MMA polymerization was performed in the same way as described for styrene. Figures 9 and 10 show the MWDs of PMMA formed under PLP conditions and simulations using the appropriate $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ and expression for $k_t(i,j)$. Again, all simulated MWDs have had Gaussian broadening added.

Russell et al.[45,46,50] have previously used eqs 3 and 4 to describe the termination rate coefficient in MMA

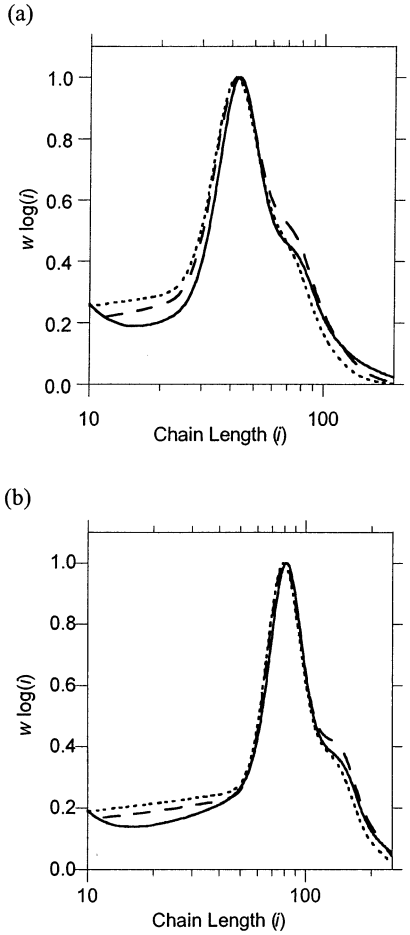

Figure 8. Comparison of experimental (—) and simulated MWDs for styrene PLP with $[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 1.26 \times 10^{-6}$ M and $k_t(i,j)$ described by the geometric mean model (α = 0.12, • • •; α = 0.16, - - -). (a) Table 2, entry 1 ($t_f = 0.1$ s); (b) Table 2, entry 3 ($t_f = 0.2$ s). Simulations: $k_t(i,j)$ given by eq 5 and parameters given in Table 3; other simulation parameters as given in Table 4.

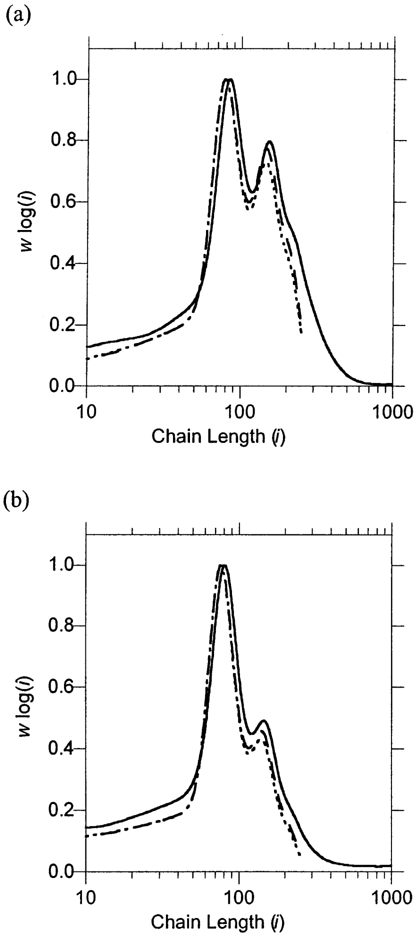

Figure 9. Comparison of experimental (—) and simulated MWDs for MMA PLP with $k_t(i,j)$ described by the Smoluchowski equation ($D_{\mathrm{mon}} = 1.5 \times 10^{-9}$, • • •; $D_{\mathrm{mon}} = 1.3 \times 10^{-9}$, - - -). (a) Table 2, entry 7 ($[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 4.3 \times 10^{-7}$ M; $t_f = 0.1$ s); (b) Table 2, entry 6 ($[\mathrm{I}^\bullet]_0^{\mathrm{av}} = 1.26 \times 10^{-6}$ M; $t_f = 0.1$ s). Simulations: $k_t(i,j)$ given by eqs 3 and 4 with parameters given in Table 3; other simulation parameters as given in Table 4.

polymerization. Table 3 shows the relevant parameters used in this study of MMA. D_{mon} was initially taken as 1.5×10^{-9} m^2 s^{-1}, the same as for styrene/benzene above; however, each simulation showed that $k_t(i,j)$ appeared to be overestimated. D_{mon} was subsequently adjusted to 1.3×10^{-9} m^2 s^{-1} to provide better fits (see Figure 9). No D_{mon} for MMA/benzene at an equivalent concentration and temperature used in this study could be found in the literature. However, it is expected that the dilution of the monomer in benzene would lead to a similar D_{mon} value as that obtained for styrene/benzene. Also, from data presented by Russell et al.,[50] it appears that the diffusion coefficients of MMA and benzene at 50 °C are similar. In any case, the adjustment of D_{mon} from 1.5×10^{-9} to 1.3×10^{-9} m^2 s^{-1} is not significant given the likely experimental error in that data. The other parameters remain the same as for the styrene case, above, with the exception of X_c that is shifted slightly toward shorter chain lengths.[50]

From Figure 9, it can be seen that the simulations tend to overestimate the dependence of $k_t(i,j)$ on chain length; i.e., the amount of high molecular weight polymer is too small in the simulation compared with the experiment. This may indicate that the parameters used in the simulations are not optimized; for example, σ could be slightly different and/or be chain length dependent, or X_c may also be different. Even given these differences, and the fact that there is no literature diffusion data for this system, the overall shape of the simulated MWDs for both primary radical concentrations reasonably approximates the experimental MWDs. Thus, the Smoluchowski equation appears to model $k_t(i,j)$ adequately for MMA polymerization under the current PLP conditions.

Mahabadi[36] also determined the geometric mean model values of k_{t0} and α for the bulk AIBN-initiated spatially intermittent polymerization of MMA at 25 °C. These were

$$k_{t0} = 1.22 \times 10^{8}\ \mathrm{M^{-1}\ s^{-1}};\quad \alpha = 0.075$$

Using these values within eq 5, simulations of the PLP–MWD experiment with the appropriate $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ values were performed and compared with the experimentally determined MWDs. The results are shown in Figure 10. Under both $[\mathrm{I}^\bullet]_0^{\mathrm{av}}$ conditions, the geometric mean model fails to give a satisfactory description of the MWD. The overall rate of termination appears to be too great in the simulation as the overtone peaks are not as significant as in the experiment. The poor fit may be due to the different polymerization conditions used in Mahabadi's experiments[36] compared with the present study. The high dilution of the monomer in benzene is the most

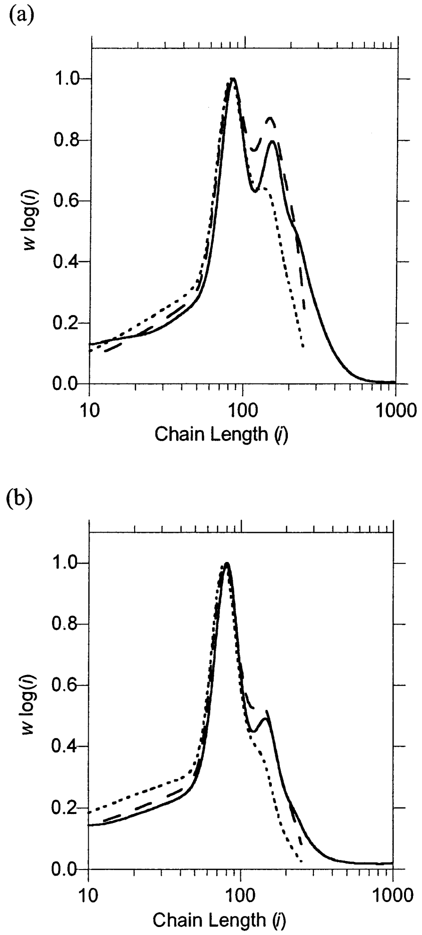

Figure 10. Comparison of experimental (—) and simulated MWDs for MMA PLP with $k_t(i,j)$ described by the geometric mean model ($\alpha = 0.075$, · · ·; $\alpha = 0.15$, - - -). (a) Table 2, entry 7 ($[I^\bullet]_0^{av} = 4.3 \times 10^{-7}$ M; $t_f = 0.1$ s); (b) Table 2, entry 6 ($[I^\bullet]_0^{av} = 1.26 \times 10^{-6}$ M; $t_f = 0.1$ s). Simulations: $k_t(i,j)$ given by eq 5 and other parameters given in Table 3; other simulation parameters as given in Table 4.

obvious difference. This may affect the diffusion characteristics of PMMA chains and thus also k_{t0} and possibly α. Therefore, one could adjust either or both k_{t0} and α and obtain reasonable fits to the experimental MWDs. Also shown in Figure 10 are simulated MWD data using the geometric mean model with $k_{t0} = 1.22 \times 10^8$ and $\alpha = 0.15$. These simulations provided a better fit to the experimental data, indicating that values within the geometric mean model are very dependent upon experimental conditions. This may be an indication that it is difficult for the geometric mean model to be used with a universal set of values for k_{t0} and α for a particular monomer.

General Comments and Comparisons. Olaj et al. (see ref 52 and citations therein) have published a number of papers on the use of the geometric mean model and have described how to estimate the parameters k_{t0} and α for a particular set of conditions. Values of k_{t0} and α for the homopolymerizations of styrene[53] ($k_{t0} = 2.3 \times 10^8$−2.7×10^8 and $\alpha = 0.16$−0.18) and MMA[54] ($k_{t0} = 1.1 \times 10^8$−1.3×10^8 and $\alpha = 0.16$−0.17) in bulk at 25 °C were reported. These values for k_{t0} and α are similar to those used in the simulations mentioned above and shown in Figure 10.

We were unable to directly apply methods suggested by Olaj et al. in the present work. The main difficulty lies with the reliable determination of the number and weight-average molecular weight for PLP samples. Even minor errors in setting the baseline can cause very large errors in the molecular weight averages and in parameter estimation. These problems are more pronounced under our polymerization conditions that lead to comparatively low molecular weights and are aggravated by very low conversions (and the consequent low sample concentrations).

We should consider the effect on our simulations of introducing a chain length dependent k_p of the form described in previous work.[18,55,56] We showed by simulation[18] that one effect of a chain length dependent k_p is to shift the value of υ_p^n by a few repeat units (because the extent of primary radical termination is reduced). For polymers of significant chain length (>50 units), this shift will be masked by experimental error. The effect on the shape of the MWD is not dissimilar to that of reducing the effective value of k_{t0}. It thus provides an explanation as to why the k_{t0} used in our simulations is less than that suggested by experimental measurements of $k_t(1,1)$ for small radicals.[51]

In relation to the determination of $k_t(i,j)$, and in particular to the discrimination of chain length dependent termination models, de Kock et al.[11] have outlined a method of examining termination kinetics through single-pulse PLP in conjunction with on-line infrared/near-infrared spectroscopy, as developed by Buback et al.[57−59] Such an experimental procedure offers the opportunity to delve into the kinetics of the termination process in greater detail. However, there are several experimental difficulties to be overcome. Foremost of these is the increase in noise as the monomer concentration decrceases. If this problem can be overcome, the method would seem to be invaluable for obtaining values of $k_t(i,i)$ as a function of chain length. In single-pulse PLP most termination is between species of similar molecular weight. Studies of low-frequency or single-pulse PLP have also been reported by Olaj et al.[60] and Buback et al.[61]

Buback and Lämmel[62] have suggested a method of extracting $\langle k_t \rangle$ data from PLP−MWD experiments. Their method relies on, in conjunction with monomer conversion measurements, fitting the ratio of the areas under the first and second PLP-generated peaks in the MWD. Other methods of determining either $\langle k_t \rangle$ or $k_t(i,j)$ through PLP are mentioned in our previous communication.[22]

Conclusions

The chain length dependence of the termination reaction in free radical polymerization has been examined. This has been achieved by comparing PLP−MWD experiments with kinetic simulations. The extension of the PLP−MWD method to give information regarding termination kinetics has been made possible by the development of a technique for determining the primary radical concentration generated per laser pulse.

Two models for the chain length dependence of the termination rate coefficients, the Smoluchowski and geometric mean models, were compared. Simulated MWD's obtained with use of a Smoluchowski model for termination provide a better fit to the experimental MWD's than those obtained using a geometric mean model. The Smoluchowski equation is implemented with experimentally measurable values of various parameters (e.g., D_{mon}), whereas the geometric mean model is more empirical in nature. The constants k_{t0} and α can only be used under the particular set of conditions from which they were determined. Therefore, it is suggested that the Smoluchowski model has greater applicability, given that D_{mon} is known.

However, while the Smoluchowski model provided good descriptions of the experimental MWDs determined in this study, the work of Russell et al.[9,46,50] suggests that a spin probability factor (p_s) could be incorporated into the model to account for the difference in $\langle k_t \rangle$ calculated from $k_t(i,j)$, and $\langle k_t \rangle$ observed experimentally. The data presented in this study indicate no need to include p_s in the Smoluchowski equation.

The use of a Smoluchowski model to describe termination in polymerization has been criticized because the translational diffusion process does not describe the motion of long polymer molecules in solution and is not an appropriate model for describing the approach of the chain ends in the rate-determining step. The geometric mean model, while empirical in origin, was thought to provide a more appropriate description. In the PLP–MWD experiment much termination is by reaction between two short chains or between short and long chains in the period immediately after the laser pulse.[18] Termination between long chains occurs in later stages of the dark period between pulses. It is possible that we need to invoke a composite expression including contributions from various forms of diffusion. However, it is not possible to test this hypothesis with the current data. In circumstances where two models provide a reasonable description of an experiment, it is clear that a combination of the two models will also provide a good description.

Acknowledgment. We thank Prof. Ken Ghiggino (School of Chemistry, The University of Melbourne) for generously allowing us to use the laser equipment. D.A.S. also thanks CSIRO Molecular Science for financial support.

References and Notes

(1) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: Oxford, 1995.
(2) Berger, K. C.; Meyerhoff, G. In *Polymer Handbook*, 3rd ed.; Brandup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; p II/67.
(3) Kamachi, M.; Yamada, B. In *Polymer Handbook*, 4th ed.; Brandup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley and Sons: New York, 1999; p II/77.
(4) Allen, P. E. M.; Patrick, C. R. *Makromol. Chem.* **1961**, *47*, 154.
(5) O'Driscoll, K. F. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: London, 1989; Vol. 3, p 161.
(6) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1959**, *81*, 1339.
(7) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
(8) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1962**, *84*, 935.
(9) Russell, G. T. *Macromol. Theory Simul.* **1995**, *4*, 497.
(10) Russell, G. T. *Macromol. Theory Simul.* **1994**, *3*, 439.
(11) de Kock, J. B. L.; Klumpermann, B.; van Herk, A. M.; German, A. L. *Macromolecules* **1997**, *30*, 6743.
(12) de Kock, J. B. L.; Van Herk, A. M.; German, A. L. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 199.
(13) Olaj, O. F.; Schnöll-Bitai, I. *Eur. Polym. J.* **1989**, *25*, 635.
(14) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.
(15) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
(16) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545.
(17) Beuermann, S.; Buback, M. *Prog. Polym. Sci.* **2002**, *27*, 191.
(18) Deady, M.; Mau, A. W. H.; Moad, G.; Spurling, T. H. *Makromol. Chem.* **1993**, *194*, 1691.
(19) Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410.
(20) Sarnecki, J.; Schweer, J. *Macromolecules* **1995**, *28*, 4080.
(21) Buback, M.; Busch, M.; Lämmel, R. A. *Macromol. Theory Simul.* **1996**, *5*, 845.
(22) Moad, G.; Shipp, D. A.; Smith, T. A.; Solomon, D. H. *Macromolecules* **1997**, *30*, 7627.
(23) Beuermann, S. *Macromolecules* **2002**, *35*, 9300.
(24) Moad, G.; Shipp, D. A.; Smith, T. A.; Solomon, D. H. *J. Phys. Chem. A* **1999**, *103*, 6580.
(25) Moad, G.; Ercole, F.; Johnson, C. H.; Krstina, J.; Moad, C. L.; Rizzardo, E.; Spurling, T. H.; Thang, S. H.; Anderson, A. G. *ACS Symp. Ser.* **1998**, *685*, 332.
(26) Doi, M. *Chem. Phys.* **1975**, *11*, 115.
(27) de Gennes, P. G. *J. Chem. Phys.* **1982**, *76*, 3316.
(28) de Gennes, P. G. *J. Chem. Phys.* **1982**, *76*, 3322.
(29) Khokhlov, A. R. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 633.
(30) Friedman, B.; O'Shaughnessy, B. *Macromolecules* **1993**, *26*, 5726.
(31) O'Shaughnessy, B.; Yu, J. *Macromolecules* **1994**, *27*, 5067.
(32) O'Shaughnessy, B. *Macromol. Theory Simul.* **1995**, *4*, 481.
(33) Yasukawa, T.; Takahashi, T.; Murakami, K. *J. Chem. Phys.* **1972**, *57*, 2591.
(34) Yasukawa, T.; Murakami, K. *Polymer* **1980**, *21*, 1423.
(35) Olaj, O. F.; Zifferer, G. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 549.
(36) Mahabadi, H.-K. *Macromolecules* **1985**, *18*, 1319.
(37) Mahabadi, H.-K. *Macromolecules* **1991**, *24*, 606.
(38) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1991.
(39) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1759.
(40) Mahabadi, H. K.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1977**, *A11*, 967.
(41) O'Neil, G. A.; Torkelson, J. M. *Macromolecules* **1999**, *32*, 411.
(42) O'Neil, G. A.; Wisnudel, M. B.; Torkelson, J. M. *Macromolecules* **1996**, *29*, 7477.
(43) Smoluchowski, M. v. *Z. Phys. Chem.* **1917**, *92*, 129.
(44) Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1984**, *88*, 2555.
(45) Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1988**, *21*, 2133.
(46) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1992**, *25*, 2459.
(47) Fischer, H.; Radom, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340.
(48) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864.
(49) Olaj, O. F.; Vana, P.; Zoder, M. *Macromolecules* **2002**, *35*, 1208.
(50) Russell, G. T.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1993**, *26*, 3538.
(51) Griller, D. In *Landolt-Bornstein, New Series*; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. II/13a, p 5.
(52) Olaj, O. F.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 697.
(53) Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 433.
(54) Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 533.
(55) Kaminsky, V.; Buback, M.; Egorov, M. *Macromol. Theory Simul.* **2002**, *11*, 128.
(56) Nikitin, A. N.; Evseev, A. V. *Macromol. Theory Simul.* **1999**, *8*, 296.
(57) Buback, M.; Hippler, H.; Schweer, J.; Vögele, H.-P. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 261.
(58) Buback, M.; Huckestein, B.; Leinhos, U. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 473.
(59) Buback, M.; Schweer, J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 145.
(60) Olaj, O. F.; Vana, P.; Kornherr, A.; Zifferer, G. *Macromol. Chem. Phys.* **1999**, *200*, 2031.
(61) Buback, M.; Busch, M.; Kowollik, C. *Macromol. Theory Simul.* **2000**, *9*, 442.
(62) Buback, M.; Lämmel, R. A. *Macromol. Theory Simul.* **1998**, *7*, 197.
(63) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *21*, 913.

MA0209951