A Theoretical Description of a Method for Model-Independent Determination of Bimolecular Chain-Length-Dependent Free-Radical-Termination Rate Coefficients

John B. L. de Kock, Bert Klumperman, Alex M. van Herk, and Anton L. German*

Laboratory of Polymer Chemistry, Eindhoven Polymer Laboratories, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT: A theoretical description is given of a method for model-independent determination of bimolecular chain-length-dependent free-radical-termination rate coefficients. By on-line determination of the monomer concentration versus time in a time-resolved pulsed laser polymerization, the value of the termination rate coefficient $k_t^{i,i}$ of the termination reaction between species of identical chain length can be determined in a very simple fashion. The key assumption in this k_t determination is that the radical chain-length distribution that is generated with a laser pulse is extremely narrow, such that all chains can be considered as being identical in chain length. With computer simulations the effects of several processes which could undermine this key assumption were investigated. For the monomer methyl methacrylate (MMA) the effects of (i) a Poisson distribution of the polymerization events, (ii) chain transfer to monomer, and (iii) the presence of a background initiation process were investigated. For MMA, none of these processes interfere with the model-independent determination of the termination rate coefficients, as long as suitable experimental conditions are chosen, which follow from the simulations.

Introduction

It has long been recognized by many authors that bimolecular free-radical termination is diffusion controlled.[1,2] This mechanism is usually envisaged as a three-stage process. It comprises the subsequent translational and segmental diffusive motion of macroradicals and finally, once the two species are in close proximity, the true termination reaction itself.[3] As a result of this diffusion-controlled nature, proper modeling of these kinetics necessitates the introduction of all parameters which can have an effect on the mobility of macroradicals in the termination rate equation. These parameters include chain length, chain flexibility, polymer−monomer−solvent interactions, radius of gyration, polymer weight fraction, viscosity, temperature, and rate coefficients of propagation and transfer. Not only are these parameters quite numerous but they are often interrelated and their exact effect on the mobility of macroradicals is simply not known. It is obvious that for this reason the modeling of termination kinetics will be an extremely complex problem to tackle. Therefore, it would be desirable if more detailed kinetic information could be obtained about this termination process,[4−6] enabling estimation of the relevance of specific parameters.

This paper will mainly focus on one of the above-mentioned parameters, i.e., the chain length of the macroradicals which are involved in the termination reaction. An effort will be made to outline a route which will give more insight into this process, with virtually no model assumptions about this dependence. This means that no input model for the chain-length dependence will be assumed for a kinetic analysis. Rather, this dependence can, in principle, be directly obtained from experimental data. Furthermore, some of the discussion will be devoted to experimental circumstances and parameters which, if not chosen correctly, can even lead to fundamentally wrong conclusions about this chain-length dependence. Before outlining this method, first the chain-length dependence of termination rate coefficients in general will be discussed, in order to get a full picture of the current kinetic "termination problem".

Chain-Length Dependence of Bimolecular Free-Radical Termination

When chain-length dependence of termination rate coefficients is discussed, a clear distinction must be made between macroscopic and microscopic rates of termination. Let $\langle k_t \rangle$ be the average (or macroscopic) rate coefficient of termination, $k_t^{i,j}$ the (microscopic) termination rate coefficient of two mutually terminating macroradicals of length i and j, respectively, $[R_i]$ the concentration of radicals of chain length i, and $[R_{tot}]$ the total radical concentration in the system. The relation between $\langle k_t \rangle$ and $k_t^{i,j}$ can then be expressed according to[7]

$$\langle k_t \rangle = \frac{\sum_i \sum_j k_t^{i,j} [R_i][R_j]}{[R_{total}]^2} \quad (1)$$

In contrast to $\langle k_t \rangle$, the $k_t^{i,j}$ values are by definition independent of radical chain-length distributions (CLD) and are therefore also independent of other kinetic parameters such as, e.g., initiator concentrations and rate coefficients for propagation and chain transfer. Although the values of $k_t^{i,j}$ can still be dependent upon a number of parameters that correlate with the physical nature of the sample (e.g., viscosity), they are less system specific than average k_t values. In studying these bimolecular termination kinetics, kineticists have developed and employed a number of basic routes (for an overview, see ref 8). Among them are steady state, decay from steady state (the so-called "aftereffect"), approach to steady state (the "preeffect"), pseudo stationary state, and "full" non-steady state, e.g., as a result of a single-pulse initiation. However, within the scope

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of this paper only two concepts will be distinguished, namely, techniques or experiments with a broad radical CLD and experiments with a narrow, preferably virtually monodisperse radical population.

Experiments that can be characterized by a broad radical CLD always result by definition in an average or a macroscopic value for the termination rate coefficient. If one would wish to describe such an experiment in terms of chain-length dependence, either a gross simplification or an almost infinite number of $k_t^{i,j}$ values would be required. In the "gross simplification" approach an analytical derivation is made, based on several assumptions, in order to reduce the number of unknown parameters in the chain-length-dependent rate equations.[9−16] Unfortunately, the assumptions used in these derivations were not validated and the choice for a particular chain-length-dependent termination model can at least be called questionable. In the numerical approach,[17−24] which has become available with the increasing speed of computers, these simplifications are not made and all possible termination events between macroradicals of different sizes are accounted for. Although this approach is physically more correct, one still needs to assume a chain-length-dependent termination model, among them the harmonic mean model,[14] the geometric mean model,[14−16,25,26] and the Smoluchowski model[27] with chain-length-dependent diffusion coefficients.[17,20] (In the numerical approach only the latter two have been used,[17−24] sometimes in combination with a chain-length-independent residual termination model.[17−19]) Besides, the discriminative value of this numerical procedure does not seem to be very significant as only one experimental parameter ($\langle k_t \rangle$ or overall polymerization rate, etc.) is available from an experiment for comparison and for justification of the termination model used, while an almost infinite number of parameters were used as input for the model. It could therefore be questioned if this is a very adequate way to deal with chain-length dependence of termination kinetics. In the authors' view, these procedures are certainly not an appropriate way to deduce (or test) new chain-length-dependent termination models.

The other technique, involving free-radical polymerizations which can be characterized by a virtually monodisperse radical CLD, is of much more interest when studying termination kinetics. Obviously, if one has a high degree of control over the radical CLD, this can significantly reduce the number of unknown parameters in a given system. A way to accomplish this is by using non-steady-state experiments in which an external source gives control over the initiation of the polymerization and therefore also over the radical CLD. The time-resolved single-pulse pulsed laser polymerization (TR-SP-PLP)[28] seems to be particularly interesting as during such an experiment a very narrow radical CLD is present. Given that chain-transfer processes or any kind of background initiation other than photoinitiation due to the laser pulse are negligible, the radical CLD can be characterized by a distribution close to a Poisson distribution. In the following section, a closer look at this technique will be presented.

Time-Resolved Single-Pulse Pulsed Laser Polymerization (TR-SP-PLP)

The TR-SP-PLP technique has been developed by the group of Buback.[28−30] As a result of a high-energy laser pulse, a high concentration of radicals is produced instantaneously out of a photoinitiator. These radicals will propagate during their lifetime. The monomer consumption as a result of this process is monitored online with near-infrared (near-IR) spectroscopy. Because of the second-order decay of the radical concentration versus time, the rate of polymerization decreases and will finally, if no other means of initiation are present, decay to zero. The kinetics of a number of monomers were investigated in this manner: ethylene,[28−31] butyl acrylate,[32,33] methyl acrylate,[34] and dodecyl acrylate.[34] To deduce kinetic parameters from the monomer consumption trace that was measured, the following kinetic scheme[28] is employed, starting at the rate of loss of radicals:

$$\frac{d[R]_t}{dt} = -2k_t[R]_t^2 \tag{2}$$

where $[R]_t$ represents the radical concentration at a certain time t after the laser pulse. The initial value of the radical concentration at $t = 0$ equals $[R]_0$, of which it is assumed that it is formed instantaneously at the exact time of the laser pulse. A constant value of k_t, from here on denoted as k_t^c (not to be confused with termination by combination) is then used to integrate the above expression and to derive the radical concentration versus time. Substitution of this concentration in the equation describing the rate of polymerization and subsequent integration result in

$$\frac{[M]_t}{[M]_0} = (2k_t^c[R]_0 t + 1)^{-k_p/2k_t^c} \tag{3}$$

where $[M]_t$ is the monomer concentration at time t and k_p the propagation rate coefficient. This equation can be used to fit experimental data from which two combined fit parameters are deduced, i.e., the product $k_t^c[R]_0$ and the ratio of k_p/k_t^c. To obtain individual rate coefficients from these two parameters, two pathways exist. One can obtain the value of k_p from other experiments (such as PLP), or one needs to have access to the maximum radical concentration at time $t = 0$ (which can be obtained from the quantum efficiency and the number of absorbed laser photons).

This kinetic scheme, however, has two major disadvantages:

(1) The obtained kinetic parameters k_p and k_t are determined as combined fit parameters, and their accuracy is dependent upon the determination of either $[R]_0$ or k_p from independent experiments.

(2) A constant value of k_t is used. If one would wish to derive eq 3 including a chain-length dependence of the termination rate coefficients, then one still has to adopt a chain-length-dependent termination model and the time elapsed after a pulse has to be coupled to a chain length. The subsequent integration steps from eq 2 to eq 3 can then lead to enormous and hard to handle mathematical expressions. (When, for instance, the geometric mean model would be applied, the integration steps can only be carried out for discrete values of the exponent α. For a definition of the geometric mean model, see eq 13.)

By looking from a somewhat different perspective at the kinetic scheme presented above, these disadvantages can be eliminated in an extremely simple fashion. By reading this scheme "backward", one does not need an estimation of $[R]_0$ but even obtains a value for this parameter directly and one does not need any model

assumptions about the chain-length dependence of the termination rate coefficient either.

The procedure is quite simple. Provided that the k_p is known, radical concentration versus time can be determined directly, according to

$$[R]_t = \frac{-\frac{d[M]_t}{dt}}{k_p[M]_t} \quad (4)$$

As the monomer concentration versus time is monitored on-line by near-IR spectroscopy, its derivative can be determined as well. A fair estimate for the concentration of radicals at time $t = 0$ can now be obtained simply by extrapolation of the calculated profile to time $t = 0$. Similar to calculating the radical concentration versus time, the termination rate coefficient can be determined, by rewriting eq 2:

$$\langle k_t \rangle = \frac{\frac{d[R]_t}{dt}}{-2[R]_t^2} \quad (5)$$

Now, if we assume that during a TR-SP-PLP experiment the radical CLD would be fully monodisperse, all macroradicals would have exactly the same length at any time. Consequently, the determined value of $\langle k_t \rangle$ in eq 5 by definition has to equal the value of $k_t^{i,i}$ at any time, in which i can then simply be coupled to time of growth t, according to

$$i = k_p[M]t \quad (6)$$

where k_p is assumed to be chain-length independent. (In the above, it was assumed that k_p was known. However, in order to determine $k_t^{i,i}$, eq 5 (again under the assumption of a fully monodisperse radical CLD) can be rewritten as

$$\frac{k_t^{i,i}}{k_p^{i}} = \frac{1}{2}\left(\frac{[M]_t[\ddot{M}]_t}{[\dot{M}]_t^2} - 1\right) \quad (7)$$

in which $[\dot{M}]_t$ represents the first derivative of the monomer concentration as a function of time and $[\ddot{M}]_t$ the second derivative. If k_p would not be known, then the ratio of $k_t^{i,i}$ and k_p can still be determined as a function of time.)

Unfortunately, a number of problems might be envisaged that could seriously undermine the most crucial and critical assumption in the procedure described above, and that is the monodispersity in the radical CLD. All processes that can somehow lead to a broadening of this radical CLD—this can occur as a result of a Poisson broadening of the polymerization events, but also can be due to transfer reactions and background initiation (either thermal of chemical) during an experiment—will violate this monodispersity assumption to some extent. (Note that microscopic values of $k_t^{i,i}$ can therefore actually never be measured.) The effect of this violation will result in an increased discrepancy between the average k_t value that is being measured and the value of $k_t^{i,i}$ that one would like to obtain. Nevertheless, it does not seem to be unreasonable that, if some broadening of this radical CLD occurs, the determined $\langle k_t \rangle$ would still be a fair measure of $k_t^{i,i}$.

Computer simulations were therefore carried out to test the sensitivity of the calculated $k_t^{i,i}$ values on a number of effects and to try to confirm the robustness of the proposed method. Last, but not least, it should be noted that the method described above only gains access to chain-length dependence of $k_t^{i,i}$ and *not* of $k_t^{i,j}$. This problem will be addressed later on.

Characteristics of Computer Simulations: Models and Parameters

The kinetic scheme used in the computer simulations in this paper comprises the following reactions:

(a) Radical generation either out of a photoinitiator as a result of an applied laser pulse or as a result of background initiation (thermal or chemical). The background initiation process is (if applied in the simulations) additional to the photoinitiation process just mentioned.

(b) Propagation with a constant value of the rate coefficient k_p. A chain-length dependence of this rate coefficient was not taken into account.

(c) Transfer to monomer with a chain-length-independent rate coefficient k_{tr}. Transfer processes to other species (polymer, initiator, solvent, etc.) were not taken into account.

(d) Bimolecular chain-length-dependent termination with a rate coefficient $k_t^{i,j}$ for the termination between an i-meric and a j-meric radical species.

To reduce the CPU time needed to simulate a TR-SP-PLP experiment, coarse graining was applied in all calculations in a fashion similar to that described by Russell et al.[17] Small radicals of different chain lengths were all treated as kinetic nonequivalent individual species and were consequently assigned to different grains. For radicals, however, with somewhat larger chain lengths, species of different lengths were simply lumped together and the average chain length was taken as the measure of the kinetic chain length of all species in that specific grain. Besides, all simulations were optimized for grain sizes (typically about 150−200 grains were used) and for time step size. The kinetic differential equations used in the computer program are given as follows:

for primary radicals which are stored in grain number 1:

$$\frac{d[R_1]}{dt} = 2fk_d[I] - k_p[M][R_1] + k_{tr}[M]([R_{tot}] - [R_1]) - 2[R_1]\sum_m k_t^{1,m}[R_m] \quad (8)$$

for all radicals not belonging to grain number 1 and not belonging to the last grain:

$$\frac{d[R_l]}{dt} = k_p[M]\left(\frac{[R_{l-1}]}{w_{l-1}} - \frac{[R_l]}{w_l}\right) - k_{tr}[M][R_1] - 2[R_l]\sum_m k_t^{l,m}[R_m] \quad (9)$$

for radicals belonging to the last grain:

$$\frac{d[R_{l_{max}}]}{dt} = k_p[M]\left(\frac{[R_{l_{max}-1}]}{w_{l_{max}-1}}\right) - k_{tr}[M][R_{l_{max}}] - 2[R_{l_{max}}]\sum_m k_t^{l_{max},m}[R_m] \quad (10)$$

in which $[R_l]$ is the total concentration of all radicals in grain number l, f the initiator efficiency, k_d the rate coefficient of dissociation of the initiator, [I] the initiator concentration, and w_l the width of grain l, which is the number of radical species of different chain length lumped together in the grain. (Note that, as the kinetic equations presented above involve grains rather than chain lengths, the symbols i and j have been replaced by l and m). For primary radicals the initial concentration at the exact moment of the laser pulse was $[R]_0$. If a background initiation was used in the simulations, then the system was first allowed to converge to a constant radical CLD before a laser pulse was "applied" to generate a high concentration of primary radicals in the system. Besides the use of coarse grains and the assumption of a non-chain-length-dependent k_p, also volume changes during the reaction were neglected. In real experimental studies, however, this should be taken into account. Furthermore, the IUPAC preferred notation[5] is used to describe the bimolecular termination reaction.

The method to determine $k_t^{i,i}$ as just proposed above claims to be model independent with respect to the chain-length dependence of termination kinetics. So, irrespective of the chain-length dependence of these termination kinetics, the proposed procedure should be able to retrieve this dependence, no matter how this dependence is reflected in an experiment. Subsequently, several models that have been frequently used in termination studies in the past, i.e., a constant value of k_t, a Smoluchowski model, and a geometric mean model, were used to test the robustness of this method. Termination by chain-length-independent reaction diffusion[35] (or residual termination) was not taken into account. The simulations presented here represent low-conversion TR-SP-PLP experiments, and therefore reaction diffusion can safely be neglected.[36]

In the Smoluchowski model[27] chain-length-dependent diffusion coefficients[17,20] were included, according to

$$k_t^{i,j} = 2\pi p_{spin}(D_i + D_j)\sigma N_A \tag{11}$$

$$D_i = \begin{cases} \dfrac{D_{mon}}{i^a} & i \le X_c \\ \dfrac{D_{mon} X_c^{\,b-a}}{i^b} & i > X_c \end{cases} \tag{12}$$

in which p_{spin} is the probability of reaction upon encounter of two radicals (as a result of spin multiplicity),[37] D_i is the diffusion coefficient for macroradicals of chain length i, σ is the capture radius of the reaction, D_{mon} is the diffusion coefficient of a monomer unit, a and b are the parameters that control the degree of chain-length dependence, and X_c represents a critical chain length at which the modeling of the diffusion coefficient of a macroradical is changed from a small-chain to a large-chain approach. Finally, the geometric mean model[14−16,25,26] was used, according to

$$k_t^{i,j} = k_t^{1,1}(ij)^{-\alpha} \tag{13}$$

in which $k_t^{1,1}$ is the termination rate coefficient for a termination reaction between two primary radicals and α is the parameter that controls the degree of the chain-length dependence. The numerical values used in the simulations can be found in Table 1.

Table 1. Input Parameters for Computer Simulations of MMA[a]

		ref
	general Parameters	
$[M]_0$/mol·L^{-1}	9.071	38
$[R]_0$/mol·L^{-1}	5×10^{-6}*	
k_p/L·mol^{-1}·s^{-1}	649	39
k_{tr}/L·mol^{-1}·s^{-1}	6.9×10^{-3}*	39, 40
$[I]_0$/mol·L^{-1}	5×10^{-3}	
k_d/s^{-1}	9.7×10^{-7}	38
f	0.72	41
T/°C	50	
w_p	0	
	Constant k_t	
k_t^c/L·mol^{-1}·s^{-1}	2×10^8	
	Smoluchowski Model	
p_{spin}	0.25	
D_{mon}/dm^2·s^{-1}	4.1×10^{-7}	42
σ/dm	5.9×10^{-9}	43
a	0.5*	21, 44−46
b	0.6*	21
X_c	86.4	21
	Geometric Mean Model	
k_t^{11}/L·mol^{-1}·s^{-1}	2×10^8	
α	0.075*	15

[a] All simulations have been performed with the above numbers, unless it is stated explicitly that other values have been used. Parameters marked with an asterisk were varied during the simulations. Only the standard values of these parameters are displayed. More details can be found in the text.

Note that several parameter values are not specific for methyl methacrylate (MMA) but have been based on styrene. However, parameters for MMA should be very close to those mentioned in the table above. The value of $k_t^{1,1}$ was set to 2×10^8 L·mol^{-1}·s^{-1}, which is slightly higher than the value reported in literature.[15] This is, however, not unreasonable as this value was determined at a slightly lower temperature.

The simulation output results consisted solely of data of the monomer concentration versus time, without any additional information that was put in the simulation program (apart from k_p). These data, which are equivalent to experimentally determined parameters in TR-SP-PLP experiments, were used to determine the termination rate coefficients as a function of the kinetic chain length. In this determination all possible effects that could have led to a broadening of the radical CLD during the TR-SP-PLP experiment were completely ignored. These results were then compared with the input termination model to check if the correct kinetic information was generated after applying the proposed method to the simulation output. Scheme 1 shows a schematic overview of the procedure that was followed.

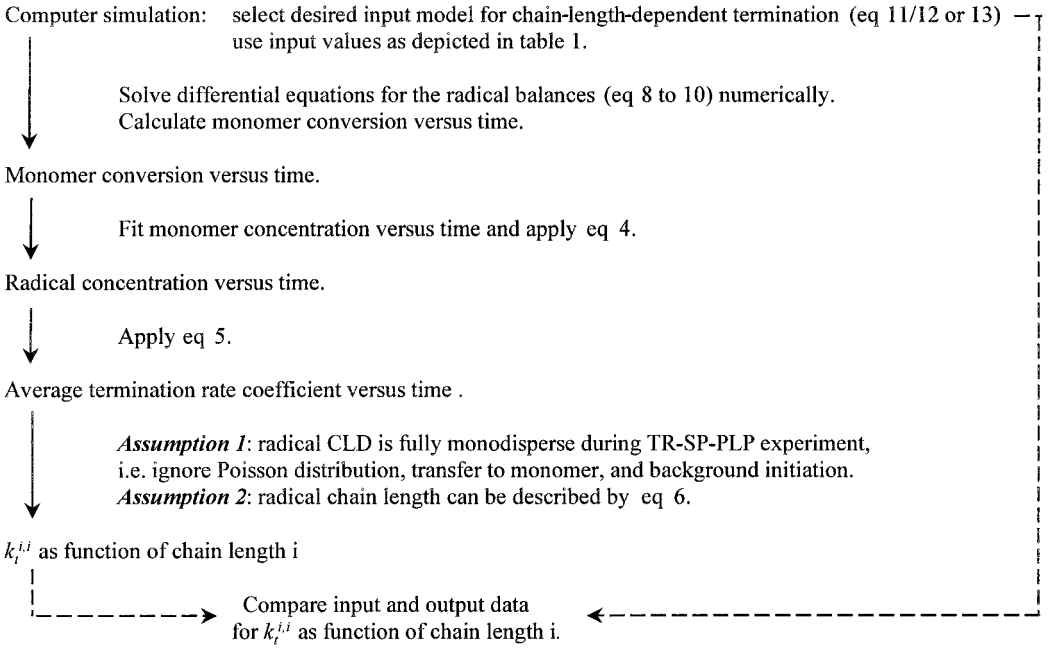
Results and Discussion

1. Example with a Constant Value of k_t: a Closer Look at the Procedure. To show the ease of the proposed method to determine termination rate coefficients, first an example with a simple kinetic scheme will be discussed. Figure 1 shows the result of a simulation with a constant value of k_t and no transfer to monomer. The relative monomer concentration versus time shows a sharp decrease at time $t = 0$, which is the exact moment when a laser flash is fired upon the monomer photoinitiator mixture.

Applying eq 4 results in the radical concentration versus time (Figure 2).

As stated before, the concentration of radicals at time $t = 0$ can now directly be determined without any

Scheme 1. Schematic Overview of the Procedure Followed in the Generation and Evaluation of the Monomer Conversion versus Time Profile for a TR-SP-PLP Experiment



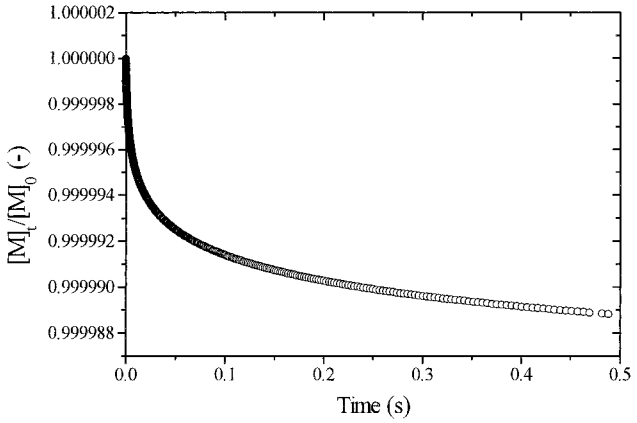


Figure 1. Monomer concentration versus time; constant value of k_t.

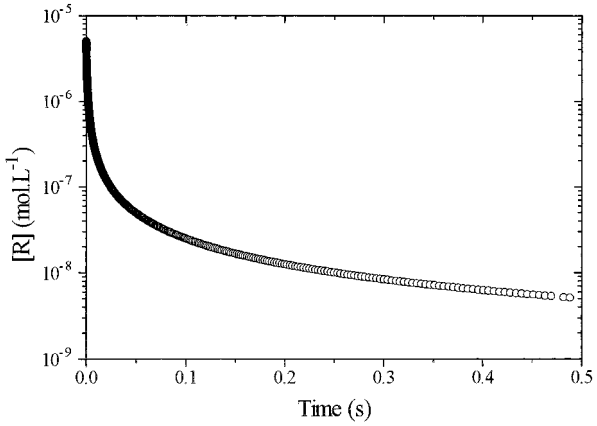


Figure 2. Radical concentration versus time; constant value of k_t.

knowledge about the initiator quantum efficiency and the number of absorbed laser photons. Note that at time $t = 0$ the first derivative of the monomer concentration is a singularity if the laser pulse and the initiator decomposition are considered as of infinitely short duration. As for an accurate determination of the derivative a few data points are necessary, a first derivative corresponding to the very first sample points cannot be gained from the method. A fairly good estimation of this radical concentration at $t = 0$ can only be determined from the extrapolation of the radical concentration to time $t = 0$. This extrapolation results in a value of $[R]_0$ of exactly 5.0×10^{-6} mol·L^{-1} which is identical with the input value as used in the simulations. (Similar numbers for $[R]_0$ can be obtained with another, closely related technique, i.e., from pulse sequence pulsed laser polymerization (PS-PLP) in conjunction with a quantitative spectroscopic analysis of the initiator end groups in the polymer.)[47]

It is important to note at this stage that the proposed method is actually a "secondary" technique in determining radical concentrations; i.e., the determination is indirect. A signal change is only generated once radicals have consumed at least one monomer unit, and this could lead to the conclusion that primary radicals that directly undergo primary radical termination remain "invisible" in this technique. However, despite the fact that TR-SP-PLP is such a secondary technique, this conclusion would be incorrect. The radical concentration is, namely, determined from the derivative of the monomer concentration versus time, and therefore we are dealing here with *rates* of polymerization reactions. For the initial rate of polymerization at time $t = 0$ all radicals that have escaped their solvent cage will contribute, whether they will initiate the polymerization or not. The extrapolation of the radical concentration versus time to $t = 0$ thus yields the total number of primary radicals having escaped their solvent cage and not only those radicals having succeeded in initiating the polymerization. In order to obtain an estimation for the initiator efficiency, the obtained estimation of $[R]_0$ should be corrected for primary radical termination, as usually this is not included in the definition of initiator efficiency.[48]

Once the radical concentration in time has been determined, the final step in determining the termination rate coefficient can be made which comprises the differentiation of this radical concentration versus time,

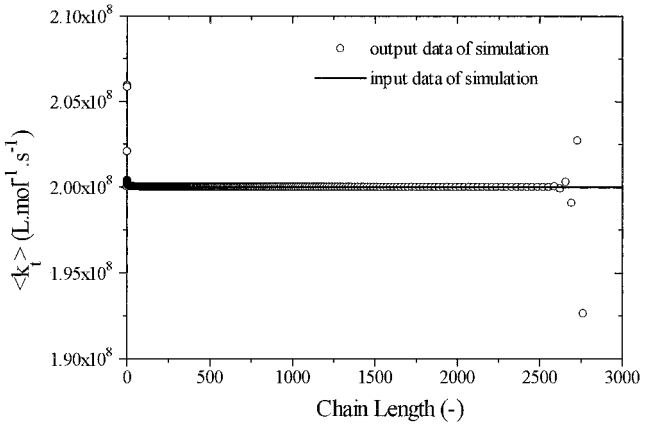


Figure 3. Termination rate coefficient versus chain length; constant value of k_t.

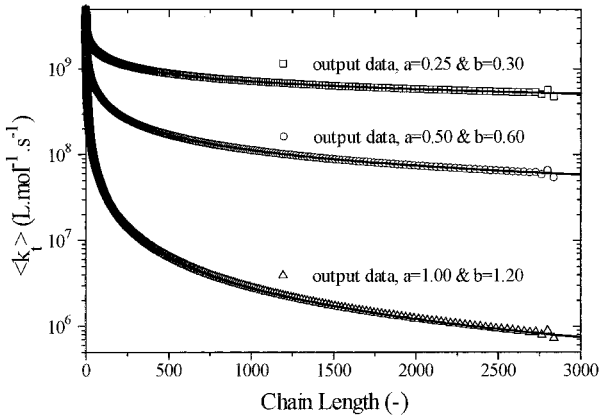


Figure 4. Termination rate coefficient versus chain length for the Smoluchowski model with Poisson broadening: variation of the chain-length-dependent coefficients *a* and *b*. The lines through the data are the corresponding input values of the simulations.

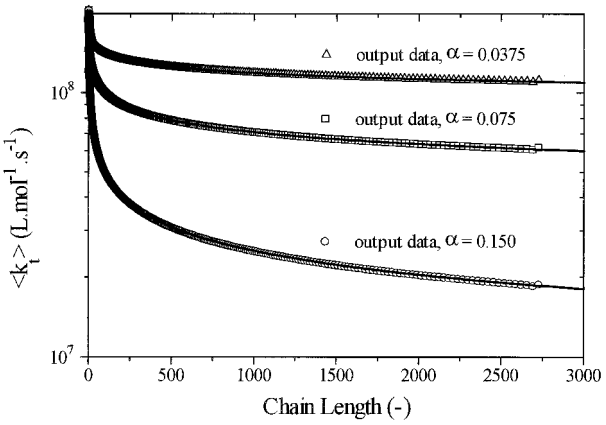


Figure 5. Termination rate coefficient versus chain length for the geometric mean model with Poisson broadening: variation of the chain-length-dependent coefficient α. The lines through the data are the corresponding input values of the simulations.

according to eq 5. In doing so, the graph in Figure 3 is obtained.

As expected, the described calculation method yields the input value of k_t. This is, of course, not very surprising, as this kinetic system can easily be solved analytically. Some scatter can be observed at both ends of the curve. This has no physical meaning but results from the simple fact that an experiment is limited to a certain time span. The curve fit procedure (which is based on a cubic spline fit) for the monomer concentration versus time is therefore less accurate at both ends of the curve compared to the intermediate part. Upon differentiation, this effect aggravates which results in scatter in the k_t data. These points will be omitted in the following graphs.

Generally speaking, the calculation of the first derivative of a given data set results in a relative noise increase compared to the original data. With respect to this it should be noted that a cubic spline fit procedure is capable of fitting quite high frequency noise. Therefore, if the experimental data are noisy, the cubic spline fit itself will be quite noisy too. Upon differentiation of the obtained spline fit, the noise increase might turn out to be too severe and hence fatal for an accurate determination of the termination rate coefficients. Besides, it should also be realized that, once a cubic spline fit is obtained for the monomer concentration versus time, this fit is partly based upon a minimization of the sum of squared errors of the monomer concentration versus time. The first derivative of the monomer concentration, however, will very probably not have the same error structure as the original data. Therefore, the first derivative of the obtained spline fit is not necessarily the best fit for the first derivative of the monomer concentration, not to mention the second derivative! Great care should thus be taken in selecting an appropriate curve fit procedure in fitting experimental data. Although the spline fit procedure performs adequately for the simulation results, it might very well be not the best choice for experimentally obtained data.

2. Calculations with No Transfer to Monomer: the Effect of Poisson Broadening. The first simulations with chain-length-dependent termination rate coefficients were performed assuming no transfer to monomer. The only physical process that can now undermine the assumption of a monodisperse radical distribution is the well-known Poisson broadening of the physical processes occurring during the polymerization, i.e., transfer, propagation, and termination (initiator decomposition was assumed to be instantaneous). This effect can be tested very simply as, by using a set of differential equations to describe the kinetics of this system, a Poisson distribution of these processes is automatically introduced.[49] This Poisson distribution, which was also present in the simulations with a constant k_t, could, of course, not interfere with those results as all radicals were assumed to have an identical mobility. Introducing a chain-length-dependent termination model will therefore enable us to envisage the effect of the Poisson broadening.

Figures 4 and 5 show the results of the simulations using a Smoluchowski model and a geometric mean model, respectively. In both simulations the chain-length dependence was varied in strength by adjusting the parameters *a* and *b* in the Smoluchowski model and the parameter α in the geometric mean model. Note that different scales have been applied in both graphs.

As can be seen in both graphs, the input and output values of the chain-length-dependent termination rate coefficients do not show any significant deviation as they lie almost exactly on top of each other. One would expect that, if a Poisson distribution is capable of undermining the assumption of $\langle k_t \rangle \approx k_t^{i,i}$, this would most likely show up in simulations with a strong chain-length dependence of the termination rate coefficient. In this case, radicals of approximately the same chain

length do *not* have approximately the same mobility and can exhibit quite different termination rate coefficients. However, as can be seen from the two graphs displayed above, even if a much stronger chain-length dependence is introduced than would be expected from literature data, no significant deviation is observed between the input and output values of k_t. A closer look at the two graphs reveals that the observed deviations are within 1% for all chain lengths. This indicates that the Poisson distribution itself does not interfere with the assumption that $\langle k_t \rangle \approx k_t^{i,i}$, even for a chain-length dependence much stronger than that now expected. The simple reason for this is that, although the broadening of the radical CLD increases upon increasing the growth time of the radicals, at the same time the change in mobility as a function of the chain length decreases exponentially. So, although for long chains the absolute broadness of the radical CLD is rather high, this has no effect on the k_t determination as all long chains have a similar diffusion coefficient. The effect of Poisson broadening will therefore be minimized.

3. Calculations with Transfer to Monomer: the Effect of Introducing Highly Mobile Species. Because of the physical nature of the transfer process, the effect of chain transfer to monomer on the "monodispersity" assumption of the radical CLD might be much more severe than the effect of the Poisson broadening. New primary radicals are formed which exhibit a much higher mobility than radicals with a larger chain length. As a result, the maximum sensible sample time in a TR-SP-PLP experiment will be limited, especially for monomers with a high transfer rate coefficient to monomer, such as MA and VAc.[38]

However, not only is the *rate of chain transfer* important but also the *strength of the chain-length dependence on the mobility of the radicals* is a key parameter in TR-SP-PLP experiments. Imagine 1000 identical radicals of moderate chain length being present at the same time in a small volume element. The average k_t of these radicals is directly related to their mobility as termination is diffusion controlled. If now only one transfer event would occur, its contribution to the average k_t of this collection of radicals will depend upon its *mobility difference* with the other radicals. If it would have a mobility which equals 1000 times that of the other radicals, then the average mobility (or the average value of k_t if the Smoluchowski model can be applied) would approximately be doubled, although the radical dispersity does hardly change! In the other extreme case, when there is no mobility difference between small and large radicals (i.e., k_t is a constant), then the overall value of k_t would not change at all.

A few simple calculations can illustrate these effects. In Figure 6 the results are shown for simulations in which the transfer rate coefficient is varied over a wide range. The Smoluchowski model is chosen to demonstrate this effect, although similar results were obtained using a geometric mean model.

As long as the transfer to monomer rate coefficient is lower than or equal to 1×10^{-2} L·mol^{-1}·s^{-1}, no deviations can be observed. The output and input values of the chain-length-dependent termination rate coefficients are about as close together as was the case for the results obtained from simulations with no transfer to monomer at all. This includes the calculated curve with a value of k_{tr} of 6.9×10^{-3} L·mol^{-1}·s^{-1}, which is the literature value of k_{tr} of MMA at 50 °C. Only at values of k_{tr} in excess of 1×10^{-1} L·mol^{-1}·s^{-1} does the

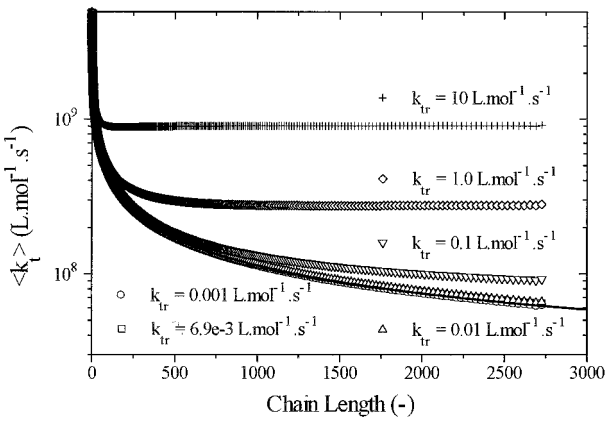


Figure 6. Termination rate coefficient versus chain length for the Smoluchowski model with Poisson broadening and transfer to monomer: variation of transfer rate coefficient. The line represents the input value of the simulations.

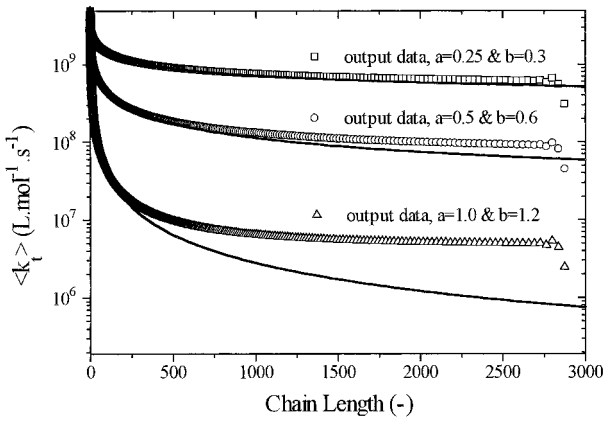


Figure 7. Termination rate coefficient versus chain length for the Smoluchowski model with Poisson broadening and transfer to monomer ($k_{tr} = 0.1$ L·mol^{-1}·s^{-1}): variation of chain-length-dependent coefficients *a* and *b*. The lines are the corresponding input values of the simulations.

procedure result in significant deviations between the input and output values.

As was speculated before, the situation becomes worse upon increasing the strength of the chain-length dependence. In Figure 7 the results are shown for a set of simulations with a constant value of k_{tr} (equal to 1.0×10^{-1} L·mol^{-1}·s^{-1} to make the effect more pronounced; see also Figure 6) but variable values of *a* and *b*, which account for the chain-length dependence in the Smoluchowski model.

From Figure 7 it can be seen directly that upon increasing the strength of the chain-length dependence of k_t, the discrepancy between input and output values of k_t increases dramatically. However, one should not forget that the curves may be somewhat misleading as a result of the logarithmic scale that is used in Figure 7. The relative difference between the input and output values of k_t increases upon increasing chain-length dependence, but the absolute difference does not.

A close look at Figure 6 reveals something peculiar. The calculation with $k_{tr} = 10$ L·mol^{-1}·s^{-1} shows a very small minimum in the obtained average k_t. Although hardly visible in Figure 6, the average k_t that resulted from the fitting procedure reaches a minimum at a chain length of approximately 170. This minimum value of k_t is about 2% less than the average k_t that was determined at chain lengths close to 3000. This deviation is outside the range of the numerical inaccuracy of the calculations.

The explanation for this seems to be quite straightforward. Upon growing of a macroradical, the change in mobility becomes less pronounced. At a certain chain length, this decay in mobility upon propagation will become so small, that this effect can be fully compensated by the gain in mobility of those radicals that undergo a transfer event. The "average mobility" of all radicals together has reached a temporary minimum and will show no further decay any more. If the macroradicals still keep on growing from that time on, the gain in mobility due to transfer even starts to be dominant over the loss of mobility due to propagation of the other chains. Consequently, a minimum can be observed in the k_t versus time graph. If this explanation were to be correct, then this observed minimum in the determined average k_t should become more and more pronounced upon increasing the value of k_{tr} and increasing the degree of the chain-length dependence of the termination rate coefficients (that is, for a termination model with a simple exponential relation between k_t and chain length). Simulations did indeed confirm this. In real experimental situations, however, the effects will probably be much smaller and details in this region (that is, the observation of a minimum) might be hard to distinguish. Nevertheless, it would certainly be interesting to see whether or not these kinds of effects would show up, e.g., by adding transfer agents to a sample prior to doing a TR-SP-PLP experiment.

The realization of the fact that transfer to monomer can be fatal for the determination of chain-length-dependent termination rate coefficients is the first step in dealing with this process. The major problem in evaluating results obtained according to the proposed method is that, at first sight, there is simply no check possible to see whether or not transfer has had an effect on the determination of the k_t values. One option that is readily available is to try to simulate the experiment with the parameters just obtained. At least a sensitivity study of the effect of transfer upon the obtained k_t should be done, similar to the figures displayed above. A high sensitivity of chain transfer to the obtained k_t data clearly indicates less reliable results.

Generally speaking, one could say that chain transfer to monomer does not have to be fatal in determining chain-length-dependent termination rate coefficients with the TR-SP-PLP technique. For a monomer with physical characteristics close to MMA, it seems to be possible to exclude the effect of transfer up to chain lengths in excess of 3000, assuming the Smoluchowski model to be correct.

4. Calculations with Transfer to Monomer and Thermal Background Initiation. Besides transfer to monomer, also a chemical or thermal background initiation might interfere with the k_t determination. Such a background initiation during a TR-SP-PLP experiment can occur as a result of different processes, e.g., the use of a monomer which is prone to spontaneous thermal initiation or the use of an initiator that can be dissociated both thermally as well as photochemically, e.g., AIBN.[50]

In the simulations, AIBN was "used" as a free-radical initiator. At 50 °C, using the values from Table 1, the flux of radicals of AIBN is approximately 7×10^{-9} mol·L^{-1}·s^{-1}. This value seems to compare quite favorably with the instantaneously formed radical concentration of 5×10^{-6} mol·L^{-1} at the instant of the laser flash. As a result of the thermal decomposition of AIBN, a steady-state polymerization is taking place before the actual laser experiment is conducted. In Figure 8 the corresponding radical concentration versus time is depicted. Note that time $t = 0$ still corresponds with the exact moment that a laser pulse is fired upon the sample. Figure 9 shows the effect of the background initiation on the k_t determination.

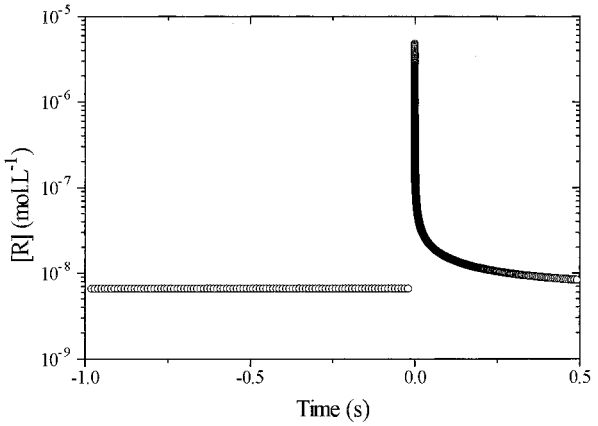


Figure 8. Radical concentration versus time for the Smoluchowski model with Poisson broadening, transfer to monomer, and thermal background initiation.

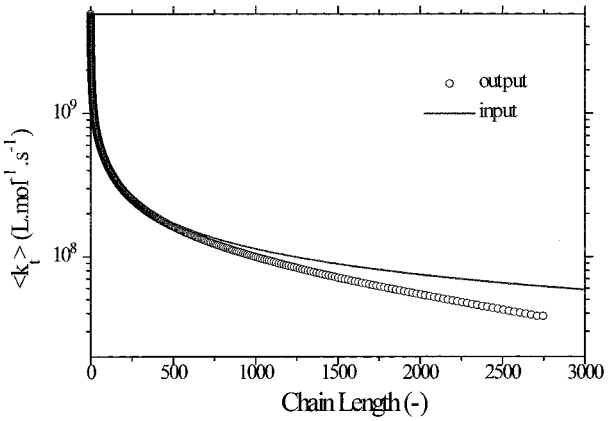


Figure 9. Termination rate coefficient versus chain length for the Smoluchowski model with Poisson broadening, transfer to monomer, and thermal background initiation. The line represents the corresponding input of the simulation.

At very small chain lengths, just after the laser pulse has been applied, the effect of a background initiation seems to be insignificant. At these very first moments directly after the laser pulse, the number of radicals that are present with a "photochemical origin" is much larger than the number of radicals present due to the background initiation process. The majority of these freshly formed radicals is so large that, even though the mobility difference between the two radical species of different origin is at maximum if the photochemically formed chains are small, the deviation in the estimated value of $k_t^{i,i}$ seems to be minimal. This is not surprising if one realizes that the interfering radical species now have a *lower* mobility instead of a *higher* mobility (as was the case for chain transfer to monomer). The only effect that a radical of a different origin than having been formed due to the laser pulse will have is that it hardly contributes to the overall high mobility. The $k_t^{i,i}$ estimation will therefore only have a relative deviation of the same order of magnitude as the fraction of "unwanted" radicals present in the polymerizing system. The introduction of less mobile species is therefore not so critical at all. No serious problems would therefore

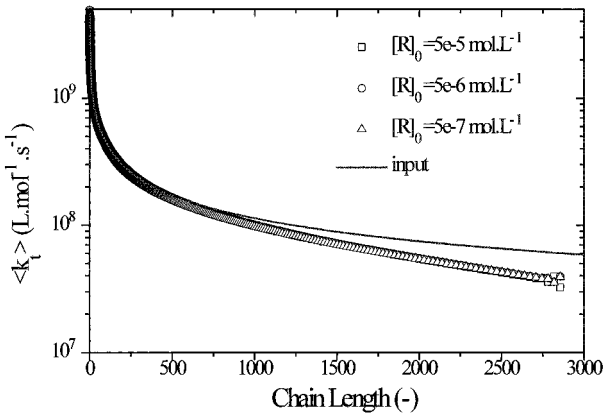


Figure 10. Termination rate coefficient versus chain length for the Smoluchowski model with Poisson broadening, transfer to monomer, thermal background initiation, and varying levels of $[R]_0$. The line represents the corresponding input of the simulations.

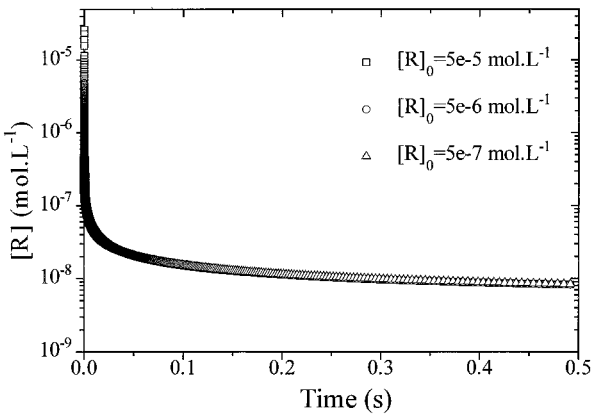


Figure 11. Radical concentration versus time for the Smoluchowski model with Poisson broadening, transfer to monomer, thermal background initiation, and varying levels of $[R]_0$.

be expected from a side reaction like chain transfer to polymer.

The situation at somewhat larger chain lengths is unfortunately less favorable. Not only are the observed deviations in this regime larger than for small chain lengths but also the estimated value of $k_t^{i,i}$ is now an *underestimation* of the true value. Because of the thermal background initiation, there is a constant flux of radicals which compensates for the loss of radicals due to termination reactions. Consequently, the decay in the total radical concentration will be less than would have been the case without a thermal background initiation. As in the kinetic scheme, only the loss of radicals is considered without taking into account the generation of new radicals; this lower decay in the radical concentration is attributed to a lower value of k_t. The closer the radical concentration approaches its original steady-state value that was present just before the laser pulse, the bigger this deviation becomes. As the polymerization proceeds and the steady-state situation is recovered, a meaningless value of 0 $L \cdot mol^{-1} \cdot s^{-1}$ would even be found for the termination rate coefficient.

To show the sensitivity of the background radical flux, two other simulations were performed which, apart from the instantaneously formed radical concentration at the moment of the laser pulse, were identical with the previous simulation. This concentration $[R]_0$ was varied 2 orders of magnitude; i.e., in one simulation it was chosen to be equal to 5×10^{-5} $mol \cdot L^{-1}$ (which is 10 times higher than the value of $[R]_0$ used in the previous simulations) and in the other simulation it was set equal to 5×10^{-7} $mol \cdot L^{-1}$ (10 times lower). Figure 10 shows the results of the $k_t^{i,i}$ determination.

Neither increasing nor decreasing $[R]_0$ seems to have any significant effect on the $k_t^{i,i}$ determination, although the fraction of "disturbing" radicals is varied over 2 orders of magnitude. The reason for this lies in the similarity of all the radical concentration profiles versus time, as depicted in Figure 11. As can be seen directly from Figure 11, these profiles are virtually identical for all input values of $[R]_0$ (apart from the starting value at time $t = 0$, of course). The initial slope of the radical concentration versus time for the simulations with the higher value of $[R]_0$ is so steep that the increase in $[R]_0$ by 1 or 2 orders of magnitude disappears almost instantaneously. The conversions obtained for all these simulations are also very similar and hardly dependent any more upon the value of $[R]_0$. (This can also be seen from the fact that the combined fit parameter $k_t^c[R]_0$ in eq 3 is not very sensitive to changes in the monomer conversion compared with the other combined fit parameter k_t^c/k_p). Adjustment of $[R]_0$ to reduce the interference of a background initiation in the k_t determination is thus a tool with limited possibilities.

Although under normal circumstances background initiation will not interfere with the k_t determination, the number of radicals generated during the dark time of an experiment should be kept as low as possible. In a TR-SP-PLP, preferably low initiator concentrations should therefore be used in conjunction with high laser pulse energies, high enough just to guarantee a sort of a minimum required value of $[R]_0$. Finally, it should be realized that the effect of background initiation is the opposite of the effect that results from chain transfer to monomer. Experimental conditions might even be chosen such that, although the assumption of monodispersity in the radical CLD is not valid at all, the effects of the background initiation and transfer to monomer process will cancel out. In that case a fairly good estimation of $k_t^{i,i}$ can still be obtained, although the experiment itself has failed.

5. TR-echo-PLP. As has been addressed before in this paper, the method described above only gains access to chain-length dependence of $k_t^{i,i}$ and not of $k_t^{i,j}$. If the Smoluchowski model, geometric mean model, or harmonic mean model (or any model with a known mathematical relation between $k_t^{i,j}$, i, and j) were to be right, then $k_t^{i,j}$ can directly be calculated from $k_t^{i,i}$ and $k_t^{j,j}$. The procedure to determine $k_t^{i,i}$ would then be one of the most effective in determining all $k_t^{i,j}$ values. Unfortunately, no unambiguous proof has ever been given for any of the above-mentioned models to be right in describing bimolecular free-radical termination kinetics, and without knowledge of this latter coefficient $k_t^{i,j}$, the determination of the coefficient $k_t^{i,i}$ is of limited value. Therefore, besides the determination of $k_t^{i,i}$, model-independent information has to be gained about the relation between $k_t^{i,j}$, $k_t^{i,i}$, and $k_t^{j,j}$. A very simple, but at the same time very interesting, experiment that might contribute to an enhanced understanding of this unknown relation might be a time-resolved "echo" pulsed laser polymerization experiment (TR-echo-PLP).

TR-echo-PLP is very similar to the TR-SP-PLP experiment, but now a second laser pulse is applied very shortly after the first one. In principle, this should result in a radical CLD that is built up of two very narrow peaks. Now, only three different termination reactions have to be distinguished: (i) the termination

between two radicals generated in pulse one, (ii) the termination between two radicals of pulse two, and (iii) a termination reaction between a radical from the first pulse and a radical from the second pulse. The rate coefficients of the first two reactions can be determined with the TR-SP-PLP method as described above, and so only the last reaction has an unknown rate coefficient. As the second pulse has a time delay compared to the first one, the number of radicals that were instantaneously formed with the first pulse has already been greatly reduced when the second pulse is applied. Besides, the second pulse introduces primary radicals to the system which will terminate at a very high rate and will probably dominate the termination process (comparable to the presence of background initiation, where the presence of large macroradicals of lower concentration has virtually no effect on k_t just after the pulse has been applied). To avoid this, the second pulse should be of much lower energy than the first one in such a way that the contribution of both radical populations present to the overall termination rate coefficient is of the same order of magnitude. The term echo refers to this much lower energy of the second laser pulse compared to the first one and to the time gap between the two pulses.

For a TR-echo-PLP experiment, rewriting of eq 1 results in

$$\langle k_t \rangle = \frac{k_t^{i,i}[R_i]^2 + k_t^{i,j}[R_i][R_j] + k_t^{j,j}[R_j]^2}{[R_{total}]^2} \qquad (14)$$

From eq 14 it can directly be seen that $k_t^{i,j}$ can only be determined if the concentrations of radicals originating from both pulses are known. This imposes serious limitations on the value of TR-echo-PLP experiments. The only time at which both radical concentrations are known is, namely, at the exact moment of the second laser pulse. At that moment the value of $k_t^{i,1}$ can be determined for a primary radical from the second pulse and a longer macroradical of length i from the first pulse. Once that number is known, the decay of both concentrations can be calculated, their new concentration can be evaluated, and subsequently the value of $k_t^{i+1,2}$ can be calculated, etc. The accuracy of this procedure will certainly decrease very rapidly with increasing chain length of both radical populations. Despite the problems involved with distracting information from a TR-echo-PLP experiment about the relation between $k_t^{i,i}$, $k_t^{j,j}$, and $k_t^{i,j}$, it might prove to be of good discriminative value in testing different $k_t^{i,j}$ models.

Conclusions

A theoretical description has been given of a method for virtually model-independent determination of bimolecular chain-length-dependent free-radical termination rate coefficients. By on-line determination of the monomer concentration versus time, the values of termination rate coefficient of the termination reaction between species of identical length can be determined in a very simple fashion. The key assumption, however, that is made in this determination is that the radical CLD that is generated with a laser pulse is so narrow that all chains can be considered as being identical in chain length. Several processes were therefore investigated which could undermine the key assumption that was made in the determination of $k_t^{i,i}$, i.e., a Poisson distribution of the polymerization events, chain transfer to monomer, and the presence of a background initiation.

The Poisson distribution, resulting in a broadening of the radical CLD, did not interfere at all with this assumption. Even up to chain lengths of approximately 3000, no significant effect was observed. Chain transfer to monomer and a background initiation, however, can impose serious limitations on the proposed procedure. The effects of both processes can be explained in terms of the fraction of radicals originating from the side reaction and the mobility difference of these species compared to the radicals which have kept on growing since they were generated with the laser pulse. Transfer to monomer results in an overestimation of $k_t^{i,i}$ as more mobile species are introduced in the system. The most pronounced effect is observed for large chain lengths. However, using numbers known from literature for the monomer MMA, no serious interference has to be expected from this side reaction. For background initiation the opposite effect is observed; that is, the value of $k_t^{i,i}$ is now an underestimation. During the polymerization, an extra radical flux compensates for the loss of radicals due to termination. As a result of this, the overall termination rate is lower than would have been the case without the thermal flux, which is attributed to a lower $k_t^{i,i}$ value. Suitable experimental conditions (e.g., low concentrations of a thermally stable initiator and high laser energy) can prevent these kinds of interferences. Finally, once the chain-length dependence of $k_t^{i,i}$ has been determined, the use of TR-echo-PLP might prove to be useful for discrimination of termination models, which relate $k_t^{i,j}$ values to $k_t^{i,i}$ and $k_t^{j,j}$ values.

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