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Chain-Length-Dependent Termination in Rotating Sector Polymerization. 2. Evaluation of the Rate Coefficient of Bimolecular Chain Termination k_t

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ABSTRACT: Chain-length distributions (CLDs) of polymers prepared by rotating-sector (RS) techniques under pseudostationary conditions were simulated for the case of chain-length-dependent termination and analyzed for their suitability of determining the rate coefficient of bimolecular chain termination k_t. This was accomplished by first calculating $\langle k_t \rangle$, the statistically correct but experimentally inaccessible "event-averaged" k_t, and checking whether a double-logarithmic plot of this quantity versus the mean chain length ν' of the radicals in the moment of their termination was able to return the exponent b of the power law characterizing the chain-length dependence introduced in the simulations. After this test had been passed successfully, the same procedure was applied to *experimentally accessible* averages of k_t such as $\overline{k_t^m}$, an average calculated from the second moment of the CLD, and $\overline{k_t^*}$, the average resulting from the rate expression for RS polymerization. Both quantities proved to be excellently suitable to give correct estimates of the average k_t characterizing a specific experiment as well as to reproduce the exponent b although a slight tendency is to be noted for $\overline{k_t^m}$ to underestimate $\langle k_t \rangle$. The results are only slightly dependent on *how* the chain-lengths of the two reacting radicals are averaged (i.e., *which* importance is assigned to the role played by the shorter one of the two chains), especially if the range of this averages is restricted to the more realistic cases. Taken in all, the determination of k_t from RS polymerization data may at least keep up with methods based on the analysis of data originating from the recently more popular pulsed-laser polymerization (PLP), especially if some care is taken with respect to the choice of experimental conditions.

Introduction

For decades, the classical rotating sector method has provided the most reliable root to the determination of individual rate constants in free radical polymerization and has entered into all relevant textbooks dealing with this subject.[1,2] Many benchmark papers were based on this method: for example, the work by Matheson et al.,[3−5] where individual rate constants of chain propagation k_p and chain termination k_t for the most important vinyl monomers, styrene, methyl methacrylate, methyl acrylate, and vinyl acetate, were given as a function of temperature; the pioneer work by Fischer et al.,[6] which established the influence of solvent viscosity on k_t and initiator efficiency f in methyl methacrylate polymerization; or, as a more recent example, the famous paper by Fukuda et al.,[7] which proved the terminal model to be inappropriate in describing the role of chain *propagation* in the copolymerization system styrene−methyl methacrylate (although the same scheme was able to describe copolymer *composition* correctly). In all of these efforts, the rotating sector method, which, according to its role of periodically combining instationary portions of rising and falling radical concentrations, in essence yields the two rate constants k_p and k_t as the ratio k_p/k_t. This was combined with the ratio k_p^2/k_t obtained from stationary polymerization experiments in order to arrive at the individual constants k_p and k_t. It was only about one decade ago when the rotating sector method began to lose ground. One reason was that the so-called pulsed-laser polymerization (PLP) was introduced as a new method into polymerization kinetics[8] that was able to produce reliable k_p data *directly* from the chain-length distribution (CLD) of a polymer prepared by applying periodic laser pulses as the initiating system (this method has developed into a benchmark procedure in the meantime[9−12]). A second argument against this classical technique arose from the fact that the termination process had been recognized meanwhile as being diffusion-controlled[13−16] (k_t being a rate *coefficient* rather than a rate constant) and, as a consequence, exhibited some chain-length dependence that put severe (and practically unfulfillable) demands on the compatibility of the data from which k_p/k_t and k_p^2/k_t had been derived. Although it had been established experimentally[17,18] and theoretically that the analysis of the CLD of polymers prepared by rotating sector polymerization (RSP) surprisingly was able to furnish k_p data with nearly the same ease as the PLP method (and a theoretical foundation for this behavior was given for chain-length *in*dependent[19] and later on, in part 1 of this series,[20] also for chain-length-dependent termination), the overwhelming majority of papers dealing with the evaluation of individual rate constants was based on the PLP technique, with no indications whatsoever of a revival of the RS technique in this modified version (preparing polymer samples and analyzing them with respect to their CLD).

Summarizing, it can be said that the problem of evaluating k_p is satisfactorily solved in the meantime, whichever method is used (PLP or RSP). In a recent effort toward the evaluation of k_t (and its chain-length dependence) in the context of PLP, we have worked out two ways of estimating *average* values of k_t as a function of chain-length, first showing the validity of these procedures by means of simulations[21,22] and afterward applying the two methods to the polymerization of

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styrene[23] and methyl methacrylate.[24] Both methods rely on assessing an average k_t for a single experiment (neglecting chain-transfer), the first one using an expression for the product of rate of polymerization v_p and weight-average degree of polymerization $\bar{P}_w$ containing k_p^2/k_t and the second one representing an expression for the rate of polymerization v_p in a pulsed-laser-initiated pseudostationary experiment that contains k_t in two different combinations, in the form k_p/k_t as well as k_t paired with the concentration of radicals produced in each laser pulse ρ. Either of the two equations had been originally derived for the case of chain-length-*in*dependent termination,[25,26] so that the k_t data represent averages defined by the method used (and to some extent also by the experimental conditions applied). The combinations of k_t with other quantities (k_p, k_p^2, or ρ) in the form of k_p^2/k_t, k_p/k_t, and $k_t\rho$, respectively, were broken into their individual parts by inserting experimental values of k_p and ρ. The average k_t data evaluated in this way finally were assigned to the length of the living chains ν' in the moment of their termination (experimentally, this quantity is connected with the number-average degree of polymerization $\bar{P}_n$ of the polymer formed). In this way, the dependence of these average k_t values on ν' could be determined experimentally,[23,24] with the results pointing to a relatively weak dependence on chain length characterized by an exponent b in the power law

$$\overline{k_t} = A'\bar{P}_n^{-b} = A\nu'^{-b} \tag{1}$$

b being in the range of 0.16−0.18 for the bulk polymerization of styrene and methyl methacrylate at 25 °C. In a recent communication,[20] we have proved that the RS polymerization may well yield practically equally good estimates of k_p when the polymers are analyzed for their CLD, even if the chain-length dependence of k_t is explicitly considered so that it appeared to be tempting to investigate whether the two methods for the evaluation of k_t described above (and used in PLP) could be modified for RSP. If this were the case, the complete evaluation of individual kinetic constants (determination of k_p and k_t, including the chain-length dependence of the latter) could be accomplished by means of the RS technique, thus making the expensive instrumentation of the laser equipment dispensable. On the basis of simulated data, it is the objective of this article to provide the proper evidence. In accordance with the experimental results cited above, the calculations are carried out for $b = 0.16$ (an exponent matching not only our experimental results[23,24] but also the numeric results[27] if the chain-length dependence is caused by a shielding effect on the end-segment caused by the overall chain in a good solvent) and for $b = 0.32$ in order to cope with the implication of a stronger chain-length dependence. A light-to-dark ratio of 1:3 was assumed throughout.

Calculational Procedure

In any case, the first step is, by proper simulation, to evaluate the CLD of active chains and dead polymer molecules for the experiment under consideration characterized by the system-dependent quantities, i.e. the propagation constant k_p, the monomer concentration $[M]$, the termination constant $k_t^{(x,y)}$ as a function of the lengths x and y of the two chains involved, and the mode of termination (disproportionation or combination), as well as the initiation profile and the duration of a period t_0 as experiment-dependent quantities. Except for the incorporation of chain-length-dependent termination, the calculations were in accordance with the method developed for initiation by arbitrary periodic initiation profiles.[28] To cope with the initiation profile the period t_0 is subdivided into L_0 intervals of equal length (running index i), L_0 being the characteristic chain length (usually identified with the position of the first point of inflection on the low-molecular-weight side of the first extra peak in the CLD of a polymer prepared under pseudostationary conditions) used for the evaluation of k_p

$$L_0 = k_p[M]t_0 \tag{2}$$

For RS polymerization it is sufficient to define a ratio r ($r = 0.25$ in this work) that marks the fraction of t_0 in which the system is illuminated. The initiation conditions, therefore, are as follows

$$[r_i] = \frac{\rho}{rL_0} \qquad 0 \le i \le rL_0 - 1 \tag{3a}$$

$$[r_i] = 0 \qquad rL_0 \le i \le L_0 - 1 \tag{3b}$$

$[r_i]$ being the concentration of primary radicals produced in the ith interval and ρ being the total concentration of primary radicals produced in the period. As not all of these quantities act independently on the CLD, it is convenient, apart from L_0, the quantity given in eq 2, to define a further dimensionless parameter C combining initiation and termination

$$C \equiv k_t^{(1,1)}\rho t_0 \tag{4}$$

Contrary to the procedure chosen earlier,[20] where the problem of k_p evaluation in RSP has been treated, the fluctuation of propagation, which mainly influences the *shape* of the CLD only, was ignored and a strict coupling of time and chain length was assumed (i.e., the chain lengths of all chains evading termination were increased automatically by one after each step). This simplification is absolutely justified with respect to those quantities that are needed in the context of the present communication and that enter into the following calculations (average rate constant of termination $\bar{k}_t$, rate of polymerization v_p, and number- and weight-average degree of polymerization, $\bar{P}_n$ and $\bar{P}_w$, respectively); they have been shown to be only very slightly affected (or to remain completely unaffected) under the influence of this assumption.[20] Starting with an approximate CLD for living radicals (e.g., the CLD for chain-length-independent termination) or developing this CLD period by period (as if establishing the pseudostationary state), the iteration process is carried out. The main point is that termination controlled by a chain-length-dependent $k_t^{(x,y)}$ given by the general equation

$$k_t^{(x,y)} = k_t^{(1,1)}\{M(\boldsymbol{t})\}^{-b} = k_t^{(1,1)}(^1/_2[x^{\boldsymbol{t}} + y^{\boldsymbol{t}}])^{-b/\boldsymbol{t}} \tag{5}$$

with $\boldsymbol{t}$ being a parameter defining the type of mean $M(\boldsymbol{t})$,[29] with $\boldsymbol{t} = -1$ denoting the harmonic mean, $\boldsymbol{t} = -b$ the so-called diffusion mean, $\boldsymbol{t} = +1$ the arithmetic mean, and $\boldsymbol{t} = -\infty$ and $+\infty$ characterizing the situation where the shorter or the longer of the two radical chains, respectively, exclusively governs the termination process. The special case $\boldsymbol{t}\rightarrow 0$ corresponds to the geometric mean

$$k_t^{(x,y)} = k_t^{(1,1)}(xy)^{-b/2} \tag{5a}$$

which is the only mean to allow a factorization of the influence of the two chains on the termination process. Thus, it is possible to study the type of the *combined* influence that is exercised by the two radicals of chain length x and y on the termination process in the most variable way. When the iteration is complete, a (periodically varying) distribution of radical chains and, as a consequence, a periodically varying overall radical concentration (all in units of ρ) are established. It is this time-averaged radical concentration $\rho m_A^{(0)}/L_0$ (given by the integral zeroth moment of the distribution of active radicals over one period $\rho m_A^{(0)}$ divided by the number of intervals L_0) that determines the rate of polymerization

$$v_p = \frac{k_p[M]}{k_t^{(1,1)}t_0}\left(m_A^{(0)}\frac{C}{L_0}\right) \tag{6}$$

$\bar{P}_n$ and $\bar{P}_w$ are calculated from the CLD of the dead polymer, which follows from the differences in the CLD of the living polymer.

In the context of studying termination, the central quantity is an “event-averaged” $\bar{k}_t$, $\langle k_t\rangle$, correctly represented by

$$\frac{\langle k_t\rangle}{k_t^{(1,1)}} = \frac{\displaystyle\sum_{i=0}^{L_0-1}\sum_{x=1}^{\infty}\sum_{y=1}^{\infty}k_t^{(x,y)}[R_{i,x}][R_{i,y}]}{\displaystyle\sum_{i=0}^{L_0-1}\sum_{x=1}^{\infty}\sum_{y=1}^{\infty}k_t^{(1,1)}[R_{i,x}][R_{i,y}]} \tag{7}$$

with $[R_{i,x}]$ and $[R_{i,y}]$ being the concentrations of radicals of lengths x and y in the ith interval, which is to be evaluated separately for each of the six values from the statistics of termination. Of course, the quantity $\langle k_t\rangle/k_t^{(1,1)}$ is not accessible experimentally. As a consequence, suitable substitutes for this (reduced) average have to be found. Two relevant possibilities may be obtained from (a) the general equation[26] for the product of rate of polymerization v_p and weight-average degree of polymerization $\bar{P}_w$ (actually, this product is the second moment of the CLD of dead polymer per time) and (b) the rate equation for RS polymerization.[1]

Both equations (originally derived for chain-length-*in*dependent termination) contain the rate constant of chain termination. If they are applied to a situation where chain-length-*dependent* termination is assumed (and chain transfer can be neglected), k_t has to be an average that is defined by the method used. We shall denote this average k_t resulting from case (a) as $\overline{k_t^m}$ and that originating from case (b) as $\overline{k_t^*}$.

The relevant equation for the first case (a) is given by

$$\bar{P}_w v_p = \frac{k_p^2}{k_t}[M]^2(3-\delta) \tag{8}$$

$[M]$ being the monomer concentration and δ representing the contribution of disproportionation to overall termination that can be easily solved for $\overline{k_t^m}$ after k_t has been replaced by this average in the case of chain-length-dependent termination

$$\overline{k_t^m} = k_p^2\frac{[M]^2(3-\delta)}{\bar{P}_w v_p} \tag{8a}$$

The well-known rate equation for RSP (for chain-length-independent termination) can be put into the form that expresses the fractional conversion per period

$$\frac{v_p}{[M]}t_0 = \frac{k_p}{k_t}\ln\left\{\frac{\sinh(t_L)}{[R_B]/[R_S]} + \cosh(t_L)\right\} \tag{9}$$

where t_L and t_D

$$t_L = rt_0/\tau_S = r\sqrt{C/r} \tag{10}$$

$$t_D = (1-r)t_0/\tau_S = (1-r)\sqrt{C/r} \tag{11}$$

are the durations of the light and the dark period, respectively, in terms of τ_S, the mean life of the radicals in a stationary polymerization with the same light intensity as in the light period of the RS experiment and distinguished by a steady-state concentration $[R_S]$

$$\tau_S^{-1} = k_t[R_S] = t_0^{-1}\sqrt{C/r} \tag{12}$$

The ratio of the “bottom” radical concentration in the radical profile $[R_B]$ in terms of $[R_S]$, $[R_B]/[R_S]$, appearing in eq 9, is given by

$$\frac{[R_B]}{[R_S]} = -{}^1/_2\frac{t_D\tanh(t_L)}{t_D+\tanh(t_L)}\left\{1-\sqrt{1+4\frac{t_D+\tanh(t_L)}{t_D^{\,2}\tanh(t_L)}}\right\} \tag{13}$$

In the case of chain-length-independent polymerization, there is only a single value for k_t. If the equations are transformed to chain-length-dependent polymerization, this k_t has to be replaced by a mean value $\overline{k_t^*}$, however, retaining the definition of parameter C in terms of $k_t^{(1,1)}$ in eq 4.

Accordingly, eqs 10−12 take the forms

$$t_L = r\sqrt{\overline{k_t^*}/k_t^{(1,1)}}\,\sqrt{C/r} \tag{10a}$$

$$t_D = (1-r)\sqrt{\overline{k_t^*}/k_t^{(1,1)}}\,\sqrt{C/r} \tag{11a}$$

$$\tau_S^{-1} = \overline{k_t^*}[R_S] = t_0^{-1}\sqrt{\overline{k_t^*}/k_t^{(1,1)}}\,\sqrt{C/r} \tag{12a}$$

Because the version of eq 9 that has been modified for chain-length-dependent termination

$$\frac{v_p}{[M]}t_0\frac{k_t^{(1,1)}}{k_p} = \left(\frac{\overline{k_t^*}}{k_t^{(1,1)}}\right)^{-1}\ln\left\{\frac{\sinh(t_L)}{[R_B]/[R_S]} + \cosh(t_L)\right\} \tag{9a}$$

is a transcendental equation in $\overline{k_t^*}/k_t^{(1,1)}$ (it contains this ratio here explicitly and in the arguments of the hyperbolic functions), the solution must be ac-

Table 1. Basic Simulation Data for Perfect Correlation between Chain Length and Time for $C = 5$ and $r = 0.25$

		$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$				$\overline{k_t^m}/k_t^{(1,1)}$		
t	L_0	dis.	dis.	comb.	$(m_A^{(0)}/L_0)C$	$\langle k_t\rangle/k_t^{(1,1)}$	dis.	comb.	$k_t^*/k_t^{(1,1)}$
					$b = 0.16$				
$-\infty$	100	54.163	2.399	1.733	2.65813	0.644	0.588	0.613	0.630
	200	113.808	2.401	1.729	2.82019	0.576	0.523	0.546	0.565
	400	240.893	2.391	1.720	2.99866	0.513	0.465	0.486	0.505
-1	100	55.768	2.409	1.747	2.73839	0.608	0.552	0.573	0.597
	200	117.308	2.410	1.743	2.90771	0.543	0.491	0.510	0.534
	400	248.471	2.400	1.733	3.09338	0.483	0.436	0.453	0.476
$-b$	100	56.788	2.432	1.775	2.78938	0.586	0.528	0.544	0.577
	200	119.632	2.430	1.770	2.96580	0.522	0.468	0.483	0.515
	400	253.653	2.418	1.759	3.15816	0.464	0.415	0.428	0.458
0	100	57.050	2.438	1.784	2.80252	0.580	0.521	0.537	0.572
	200	120.242	2.437	1.779	2.98106	0.517	0.462	0.476	0.510
	400	255.033	2.424	1.768	3.17541	0.459	0.409	0.422	0.454
$+1$	100	58.302	2.468	1.820	2.86509	0.555	0.493	0.504	0.549
	200	123.078	2.464	1.814	3.05194	0.493	0.436	0.445	0.489
	400	261.327	2.449	1.802	3.25408	0.437	0.386	0.394	0.434
$+\infty$	100	59.987	2.483	1.837	2.94934	0.525	0.463	0.471	0.520
	200	126.737	2.477	1.830	3.14343	0.466	0.409	0.416	0.462
	400	269.224	2.462	1.818	3.35280	0.412	0.362	0.368	0.410
					$b = 0.32$				
$-\infty$	100	70.517	2.525	1.741	3.47583	0.393	0.330	0.360	0.383
	200	158.556	2.523	1.732	3.93891	0.309	0.257	0.281	0.303
	400	359.607	2.511	1.719	4.48259	0.240	0.199	0.218	0.237
-1	100	75.727	2.554	1.774	3.73635	0.341	0.282	0.306	0.335
	200	170.828	2.547	1.762	4.24570	0.267	0.219	0.238	0.263
	400	388.274	2.532	1.748	4.84093	0.207	0.169	0.184	0.204
$-b$	100	78.641	2.597	1.823	3.88205	0.316	0.258	0.276	0.311
	200	177.999	2.584	1.809	4.42498	0.246	0.199	0.213	0.243
	400	405.519	2.563	1.792	5.05649	0.190	0.153	0.165	0.188
0	100	80.639	2.635	1.866	3.98195	0.301	0.241	0.257	0.297
	200	183.020	2.619	1.851	4.55051	0.232	0.185	0.197	0.230
	400	417.779	2.595	1.832	5.20974	0.179	0.143	0.152	0.177
$+1$	100	85.320	2.722	1.961	4.21601	0.268	0.209	0.218	0.266
	200	194.401	2.698	1.940	4.83501	0.206	0.160	0.167	0.205
	400	444.868	2.665	1.916	5.54835	0.158	0.122	0.128	0.157
$+\infty$	100	91.242	2.771	2.008	4.51208	0.235	0.179	0.186	0.234
	200	208.244	2.742	1.985	5.18110	0.180	0.137	0.142	0.179
	400	477.034	2.707	1.959	5.95042	0.137	0.105	0.109	0.137

complished by numeric methods in this case. In practice, the left-hand side of eq 9a is replaced by $m_A^{(0)}C/L_0$ (eq 6).

Results and Discussion

The main concern of this communication is a 4-fold one:

1. Is the power law with reference to the chain lengths x and y of the two living chains undergoing termination, eq 5, which has been inserted for $k_t^{(x,y)}$ into the calculations, transposed into a similar power law (of the type given by eq 1) when the (theoretical) event-weighted mean of the termination coefficient $\langle k_t\rangle$ is calculated as a function of the average chain length of living chains ν' in the moment of their termination?
2. Is the same true for the two experimentally accessible average k_t values, $\overline{k_t^m}$ and $\overline{k_t^*}$?
3. Is the value of the exponent b in eq 5 that has been inserted in the calculations recovered in an equation of the form of eq 1, and how does the prefactor of these equations match with the prefactor of eq 5 (which equals unity)?
4. What is the influence of the parameter $\boldsymbol{t}$ governing the type of averaging the chain lengths x and y of the two chains involved in the termination process?

The data necessary to answer these questions are compiled in Table 1. One entry in Table 1 also refers to the quantity $(m_A^{(0)}/L_0)C$ that describes the rate of polymerization v_p. As an example, the behavior of $\langle k_t\rangle/k_t^{(1,1)}$ is represented graphically in Figure 1 for all six values of the parameter $\boldsymbol{t}$ ($=-\infty$, -1, $-b$, $\rightarrow 0$, $+1$, and $+\infty$) as a function of ν' on a double-logarithmic scale (ν' is identical with $\bar{P}_n$ for termination by disproportionation and equals $\bar{P}_n/2$ for termination by combination). In Figure 2, equivalent plots are shown for $\overline{k_t^*}/k_t^{(1,1)}$ and $\overline{k_t^m}/k_t^{(1,1)}$, the latter one for termination by disproportionation *and* combination, for the special case $\boldsymbol{t} = -b$. The values obtained for the preexponential factor A and those recovered for the exponent b are summarized in Table 2. For reasons of simplicity and better comparability with PLP results, the variation of ν' was achieved by varying L_0 at a constant value of the parameter C, $C = 5$. Translated to an experimental procedure, this would mean that the sensitizer concentration should be chosen as inversely proportional to L_0. In practice, this does not mean any restriction, as essentially the same results will be obtained if L_0 (t_0 in the experiment) is varied at *constant* sensitizer concentration.

Event-Weighted Average $\langle k_t\rangle$. This type of average (as it should, of course) is able to reproduce the exponent b in an excellent manner, with the values ranging from 0.152 to 0.161 for a value of $b = 0.16$ and from 0.303 to 0.326 for a preset value of $b = 0.32$, depending on the type of mean chosen (the lower value always corresponding to $\boldsymbol{t} = -\infty$ and the higher one to $\boldsymbol{t} = +\infty$). Interestingly, the best accordance with the theoretical

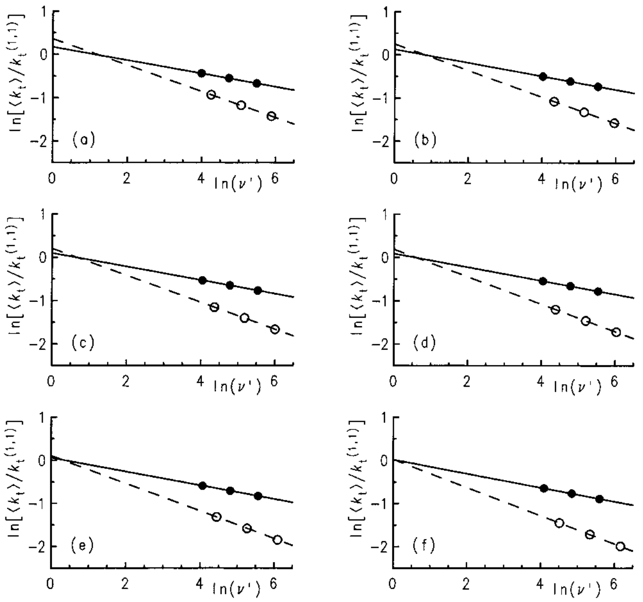

Figure 1. Double-logarithmic plots of $\langle k_t\rangle/k_t^{(1,1)}$ vs the chain length in the moment of termination ν' for $b = 0.16$ (filled symbols, full lines) and $b = 0.32$ (open symbols, broken lines) calculated by use of parameters $r = 0.25$, $C = 5$, and $\boldsymbol{t} = -\infty$ (a), −1 (b),−*b* (c), →0 (d), +1 (e), and +∞ (f). The straight lines result from linear regression.

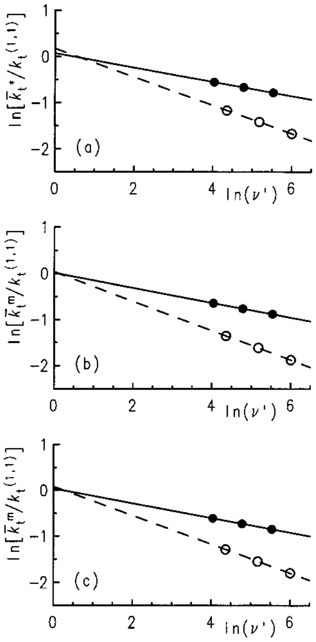

Figure 2. Double-logarithmic plots of $\overline{k_t^*}/k_t^{(1,1)}$ (a) and $\overline{k_t^m}/k_t^{(1,1)}$ for termination by disproportionation (b) and combination (c) vs the chain length in the moment of termination ν' calculated by use of parameters $r = 0.25$, $C = 5$, and $\boldsymbol{t} = -b$. Symbols as in Figure 1.

value is given by the (physically unrealistic) arithmetic mean, $\boldsymbol{t} = +1$. The preexponential factor *A* exhibits the opposite tendency: it is highest for $\boldsymbol{t} = -\infty$ and lowest for $\boldsymbol{t} = +\infty$. The overall span, however, is comparatively small and is about 17% for $b = 0.16$ and about 40% for $b = 0.32$, with *A* being of the order of unity throughout.

Experimentally Accessible Averages $\overline{k_t^m}$ and $\overline{k_t^*}$. As can be deduced from the data listed in Table 1, $\overline{k_t^m}$ underestimates $\langle k_t\rangle$ by about 10% for $b = 0.16$ (by about 20% for $b = 0.32$) for termination by disproportionation and a little less for termination by combination. This is an observation which is well-known from numerical studies on PLP.[21] Apart from this deviation, the exponent *b* is recovered in a satisfactory manner, with *b* ranging from 0.156 to 0.164 ($b = 0.16$) and from 0.308 to 0.323 ($b = 0.32$) with practically no differences caused by the mode of termination. Again, the recovered exponents increase slightly with increasing parameter $\boldsymbol{t}$. The preexponentials *A* accordingly are slightly less than those registered for $\langle k_t\rangle$. $\overline{k_t^*}$ is a still-better estimate for $\langle k_t\rangle$: the deviations do not exceed 2% ($b = 0.16$) or 3% ($b = 0.32$), respectively, in the worst case ($\boldsymbol{t} = -\infty$). There is a slight tendency to underestimate the parameter *b*; the recovered values ranging from 0.148 to 0.158 ($b = 0.16$) and from 0.295 to 0.324 ($b = 0.32$), in the same order as those observed for $\langle k_t\rangle$ and $\overline{k_t^m}$. The preexponentials *A* are rather close to those obtained for $\langle k_t\rangle$.

Table 2. Prefactor *A* and Exponent *b* Obtained by Double-Logarithmic Plots for the Various Averages of k_t using the Data Given in Table 1

	$\langle k_t\rangle/k_t^{(1,1)}$		$\overline{k_t^m}/k_t^{(1,1)}$ dis.		$\overline{k_t^m}/k_t^{(1,1)}$ comb.		$\overline{k_t^*}/k_t^{(1,1)}$	
t	*A*	*b*	*A*	*b*	*A*	*b*	*A*	*b*
				$b = 0.16$				
−∞	1.184	0.152	1.101	0.157	1.141	0.156	1.139	0.148
−1	1.130	0.154	1.042	0.158	1.079	0.157	1.099	0.152
−*b*	1.101	0.156	1.011	0.161	1.039	0.160	1.077	0.154
0	1.092	0.156	1.002	0.162	1.029	0.161	1.068	0.154
+1	1.061	0.159	0.956	0.163	0.982	0.164	1.039	0.157
+∞	1.017	0.161	0.905	0.164	0.923	0.164	0.994	0.158
				$b = 0.32$				
−∞	1.428	0.303	1.238	0.310	1.335	0.308	1.344	0.295
−1	1.280	0.305	1.094	0.313	1.177	0.311	1.247	0.303
−*b*	1.225	0.310	1.037	0.319	1.084	0.314	1.189	0.307
0	1.204	0.316	0.969	0.317	1.042	0.319	1.183	0.315
+1	1.112	0.320	0.891	0.326	0.914	0.322	1.101	0.319
+∞	1.025	0.326	0.767	0.322	0.799	0.323	1.008	0.324

As a matter of fact, numerical studies always have to use reduced quantities. Thus, all k_t values are given in multiples of $k_t^{(1,1)}$. For the evaluation of $\overline{k_t^m}/k_t^{(1,1)}$, two routes are possible: Either the ratio of the second moments of the CLD for $b = 0$ and $b \neq 0$ is calculated (see eq 8a from Olaj et al.[21]) or the right-hand side of eq 8 is rewritten in form of the (reduced) parameters *C* and L_0. This, of course, yields a term that corresponds to the *long-chain limit* of the second moment for the hypothetical case of chain-length-independent termination. To avoid merging data subject to different degrees of short-chain effects, the former route (which has been already applied to laser-pulse polymerization[21]) was used although the latter one more closely resembles the experimental situation (where eq 8 is directly used, ignoring the fact that eq 8 is strictly valid in the long-chain limit only). By means of the second route, slightly smaller values of $\overline{k_t^m}/k_t^{(1,1)}$ are found, with the reduction being more pronounced the smaller the L_0. This in turn results in a slight but significant decrease of exponents and prefactors.

Influence of the Parameter *t* Characterizing the Type of Mean. Some of the features caused by the different possibilities of averaging the two chain lengths *x* and *y* of the two chains involved in the termination process have already been mentioned above. Although the term "short−long termination" is a very popular one in the field of chain-length-dependent termination in free radical polymerization, a choice of $\boldsymbol{t} = -\infty$ (when the termination process is exclusively governed by the shorter of the two chains) is not realistic (the same, of course, refers to its counterpart, $\boldsymbol{t} = +\infty$, too) and is included for reasons of completeness only. The realistic range of $\boldsymbol{t}$ parameters probably is restricted to $-1 \leq \boldsymbol{t} \leq 0$, which also includes the so-called diffusion mean $\boldsymbol{t} = -b$ for all reasonable values of b. Actually, this mean corresponds to the averaging of the two diffusion coefficients in the rate expression for a diffusion-controlled bimolecular reaction if the diffusion coefficients go with P^{-b}. There would be no ambiguity whatsoever if values in the range of 0.5−0.6 were experimentally found for the b parameter because these would characterize the dependence of the diffusion coefficients on the degree of polymerization P of the chain molecules.

Khokhlov,[30] on the basis of arguments derived from statistical mechanics, has favored the harmonic mean ($\boldsymbol{t} = -1$) with a value of $b = 0.16$ obtained from scaling theory for *chemically* controlled bimolecular reactions. Curiously enough, this would impart an even more important role to the shorter chain than is characteristic of the genuine diffusion mean ($\boldsymbol{t} = -b$). At least for low values of parameter b, as they have been observed experimentally, the diffusion mean would differ only slightly from the geometric mean ($\boldsymbol{t} \rightarrow 0$) which is much more comfortable in all calculations because the contributions of the two chains are easily factorized. Within the rather narrow range of reasonable $\boldsymbol{t}$ parameters remaining ($-1 \leq \boldsymbol{t} \leq 0$), there is practically no variation of the results, for neither $\langle k_t \rangle$ nor $\overline{k_t^m}$ and $\overline{k_t^*}$ so that the choice of the type of mean does not appear to play an important role, at least for the weak chain-length dependencies observed experimentally.[23,24]

Comparison with PLP Results. Some experience has already been collected with PLP data, with respect to the chances of representing k_t by suitable averages,[21,22] as well as with respect to the type of mean to be used.[31] By and large, the results are absolutely comparable, differences being of quantitative character only. One point to be mentioned is that for $\langle k_t \rangle$ the b values recovered extend up to 0.175 in the case of $b = 0.16$ and up to 0.344 in the case of $b = 0.32$. On the whole, $\langle k_t \rangle$ even appears to be reproduced a little more correctly in RSP compared to that from PLP. This is also reflected in an even better agreement between preset and recovered exponents in the relevant range of $\boldsymbol{t}$ parameters ($-1 \leq \boldsymbol{t} \leq 0$). This might be a consequence of the lower dispersity in the chain-length distribution of active radicals and dead polymer in the case of RSP in comparison to PLP.

Experimental Relevance. As already mentioned, all calculations were carried out with a constant value of $C = 5$ for varied t_0 (or L_0). This is not really the way RS experiments are usually performed (normally, the sector speed is varied and the sensitizer concentration is kept constant, which would correspond to varying L_0 at constant C/L_0^2). From PLP experiments, it is known that the parameters of the double-logarithmic plots of average k_t values versus ν' are only very slightly influenced if data sets originating from various C parameters are used. To demonstrate this fact also for RSP, data calculated for $\boldsymbol{t} \rightarrow 0$ (geometric mean approximation) extending to rather high degrees of polymerization (up to 8000) and various C parameters ($1 \leq C \leq 10$) are shown in form of double-logarithmic plots versus ν' in Figure 3 for $\langle k_t \rangle / k_t^{(1,1)}$, $\overline{k_t^*}/k_t^{(1,1)}$, and $\overline{k_t^m}/k_t^{(1,1)}$, the latter quantity being for disproportionation as well as for combination. All plots exhibit a (close to) perfect linearity and the (negative) slopes of the plot (b), which are shown in the diagrams, agree excellently with those given in Table 2 for $\boldsymbol{t} \rightarrow 0$.

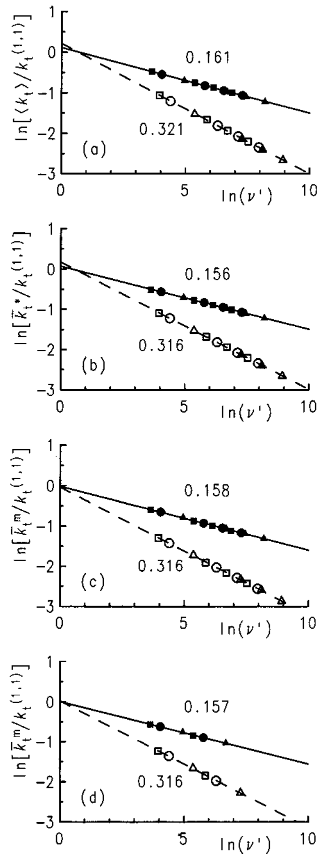

Figure 3. Double-logarithmic plots of $\langle k_t \rangle / k_t^{(1,1)}$ (a) $\overline{k_t^*}/k_t^{(1,1)}$ (b) and $\overline{k_t^m}/k_t^{(1,1)}$ for termination by disproportionation (c) and combination (d) vs the chain length in the moment of termination ν' for $b = 0.16$ (filled symbols, full lines) and $b = 0.32$ (open symbols, broken lines) calculated by use of parameters $\boldsymbol{t} \rightarrow 0$ and $C = 1$ (triangles), 5 (circles), and 10 (squares) for $r = 0.25$ and $L_0 = 100$, 500, 1000, and 2000 (a, b, and c) or 100 and 500 (d). The straight lines result from linear regression, with the (negative) slopes being given in the diagrams.

Conclusions

From all this, it may be easily deduced that RSP provides an equally convenient and reliable access to the determination of k_t and its chain-length dependence as the more costly PLP. There appear to exist even some slight advantages of RSP over PLP that may be traced back to the lower polydispersity in RSP, especially with respect to the active chains. Hopefully, this can induce a revival of RSP.

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References and Notes

(1) Bamford, C. H.; Barb, W. G.; Jenkins, A. D.; Onyon, P. F. *The Kinetics of Vinyl Polymerization by Radical Mechanisms*; Butterworth: London, 1958; Chapter 2.
(2) Bovey, F. A., Winslow, F. H., Eds. *Macromolecules, An Introduction to Polymer Science*; Academic Press: NewYork, 1979; Chapter 2.

(3) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1949**, *71*, 497.
(4) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1949**, *71*, 2610.
(5) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 1700; 5395.
(6) Fischer, J. P.; Mücke, G.; Schulz, G. V. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 154.
(7) Fukuda, T.; Ma, Y.-D.; Inagaki, H. *Macromolecules* **1985**, *18*, 17.
(8) (a) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987,** *188*, 1689. (b) Olaj, O. F.; Bitai, I. *Angew. Makromol. Chem.* **1987**, *155*, 177.
(9) Buback, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 293.
(10) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 851.
(11) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. T.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
(12) 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.
(13) Schulz, G. V. *Z. Phys. Chem.* **1956**, *8*, 284.
(14) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1959**, *81*, 1339.
(15) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
(16) Allen, P. E.; Patrick, C. *Makromol. Chem.* **1961**, *47*, 154; **1964**, *72*, 106.
(17) Olaj, O. F.; Kremminger, P.; Schnöll-Bitai, I. *Makromol. Chem.* **1988**, *9*, 771.
(18) Olaj, O. F.; Schnöll-Bitai, I.; Kremminger, P. *Eur. Polym. J.* **1988**, *25*, 535.
(19) Zifferer, G.; Olaj, O. F. *Makromol. Chem.* **1990,** *191*, 1699.
(20) Olaj, O. F.; Kornherr, A.; Zifferer, G. *Macromol. Theory Simul.* **1999**, *8*, 561.
(21) Olaj, O. F.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **1997**, *18*, 997.
(22) Olaj, O. F.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **1998**, *19*, 89.
(23) Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 433.
(24) Olaj, O. F.; Vana, P. *Macromol. Rapid Commun.* **1998**, *19*, 533.
(25) Olaj, O. F.; Bitai, I.; Gleixner, G. *Makromol. Chem.* **1985**, *186*, 2569.
(26) Olaj, O. F.; Zifferer, G. *Eur. Polym. J.* **1989**, *25*, 961.
(27) Olaj, O. F.; Zifferer, G. *Makromol. Chem.* **1988**, *189*, 1097.
(28) Olaj, O. F.; Zifferer, G. *Makromol. Chem., Theory Simul.* **1992**, *1*, 71.
(29) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1972; Chapter 3, p 10.
(30) Khokhlov, A. R. *Macromol. Chem., Rapid Commun.* **1981**, *2*, 633.
(31) Olaj, O. F.; Kornherr, A.; Zifferer, G. *Macromol. Theory Simul.* **1998**, *7*, 501.

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