# Termination Processes in Free Radical Polymerization. 8. Complete Treatment of a Kinetic Scheme Comprising Chain Length Dependent Termination in Terms of Closed and Approximate Closed Expressions Based on the Geometric Mean Assumption†

**Oskar Friedrich Olaj,* Gerhard Zifferer, and Günther Gleixner**

*Institute of Physical Chemistry, University of Vienna, A-1090 Vienna, Austria.*
*Received April 28, 1986*

ABSTRACT: In the frame of the so-called geometric mean approximation, which relates the rate constant of bimolecular termination $k_t$ to the length of the two radical chains $x$ and $y$ involved in the termination process by $k_t = k_t^\circ(xy)^{-b/2}$ (with $k_t^\circ$ being a constant and $b$ characterizing the extent of the chain length dependence of termination), a concept has been worked out that allows a complete treatment of a kinetic scheme comprising initiation, propagation, chain transfer, termination by disproportionation, and/or recombination. This treatment is based on exact closed expressions for the degrees of polymerization for disproportionation- and/or recombination-terminated polymer (in the absence of chain transfer) and on extremely good closed approximate expressions in the case of (additional) occurrence of chain-transfer reactions. Furthermore, an approximate closed expression has been derived for the chain length distribution of dead polymer fully or partly terminated by recombination which may be also used for the evaluation of the viscosity-average degree of polymerization. The resulting expressions are analyzed with respect to their experimental implications.

## I. Introduction

Although the mutual termination between two growing chains in free radical polymerization has long been recognized as a rather complicated and diffusion-controlled process,[1-4] for decades the overwhelming majority of scientists working in this field have been content with assigning to this reaction a single rate constant independent of the length of the two chain radicals involved in the termination process. It is only relatively recently that new experimental techniques[5] or careful and critical reexamination of older experiments and/or critical application of older techniques[6-8] have cast some doubt on this rather comfortable assumption and have revealed that most probably there is a slight but significant dependence of the rate constant of bimolecular chain termination $k_t$ on radical chain length.

In the course of these new investigations a simple power law of the form[6,9]

$$k_t = k_t^\circ(\overline{x,y})^{-b} \tag{1}$$

has been proposed for the chain length dependence of $k_t$, where $(\overline{x,y})$ is some mean of the chain lengths of the two radicals $R_x$ and $R_y$ taking part in the termination process and $k_t^\circ$ is a constant assumed to be the rate constant characteristic of the termination reaction between two radicals of unity degree of polymerization.

It is easy to foresee that most of the familiar relationships established for chain length independent termination will be heavily affected if $k_t$ actually turns out to be chain length dependent. Many calculations have been carried out in order to obtain an impression of how the dependence of the degree of polymerization of dead polymer $P$, rate of polymerization $v_p$, and kinetic chain length $\nu$ on rate of initiation $v_0$ will develop when the chain length dependence of $k_t$ actually is given by an equation like eq 1.

So, numerical solutions, which may be obtained for any value of the exponent $b$ and in principle also for any type of mean $(\overline{x,y})$, have been provided for kinetic schemes comprising termination by disproportionation or recombination,[9,10] and termination by disproportionation together with chain transfer.[11] In all these cases not only the (by far) more convenient "geometric mean assumption"

$$(\overline{x,y}) = (xy)^{1/2} \tag{2}$$

but also the more complicated "harmonic mean assumption"

$$(\overline{x,y}) = 2xy/(x + y) \tag{3}$$

has been used, which most probably, as is shown theoretically[12] and numerically,[13] gives the more appropriate functional description of how the chain lengths $x$ and $y$ of the two radicals, $R_x$ and $R_y$, which are involved in the termination reaction, influence the probability of the two chain ends to come into contact with each other, at least if the termination process is preceded by an equilibrium pair conformation of the two chain radicals.

These calculations have invariably started with the cyclic definition of the propagation probability of a radical chain of length $x$

$$\alpha_x = \left(1 + \frac{k_{tr}[T]}{k_p[M]} + \frac{k_t^\circ}{k_p[M]}\sum_y F(x,y)[R_0]\prod_{i=1}^{y}\alpha_i\right)^{-1} \tag{4}$$

where $F(x,y)$ in a general way describes the functional dependence of $k_t$ on the chain lengths $x$ and $y$ of the two radicals involved in the termination process, $k_t = k_t^\circ F(x,y)$; $k_p$ and $k_{tr}$ are the (bimolecular) and chain length independent rate constants of chain propagation and chain transfer to T, [M] and [T] are the concentrations of monomer and chain-transfer agent, respectively, and $[R_0]$ is the concentration of radicals having "zero degree of polymerization" (this means not only of the primary radicals in the strict sense which are formed by decay of initiator but also of those radicals which result from the transfer reaction to the transfer agent T). No distinction is made between these two "kinds" of radicals, which are assumed to transform quantitatively into $R_1$ radicals by monomer addition with the same rate constant $k_p$, which characterizes the propagation rate of chain radicals ($x \geq 1$).

† Affectionately dedicated to Prof. Dr. A. Neckel, Institute of Physical Chemistry, University of Vienna, on occasion of his 60th birthday, together with our best wishes.

0024-9297/87/2220-0839$01.50/0 

On applying the geometric mean approximation

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

$x^{-b/2}$ can be extracted from the sum contained in eq 4 and a convenient expression for $\alpha_x$ is obtained immediately[9,14]

$$\alpha_x = (1 + Cx^{-b/2} + D)^{-1} \tag{4a}$$

with $C$ being the reciprocal of $\nu_0$, the kinetic chain length that would be obtained if the polymerization proceeded at the same rate of initiation $v_0$ with a chain length independent $k_t = k_t°$, and $D$ being the so-called transfer term, $D = k_{tr}[T]/k_p[M]$.

With the harmonic mean assumption (or any other type of mean) the complete set of $\alpha_x$ values has to be evaluated by an iterative process. As a final step, all important kinetic quantities may be derived from these $\alpha_x$ values.[9-11,14]

Closed solutions for chain length dependent $k_t$ are accessible under extremely special conditions only, which, in addition, mostly refer to unrealistic values of the exponent $b$. However, general favorable prospects are offered if the expression obtained for $\alpha_x$ using the geometric mean assumption, eq 4a, is transformed into its long-chain limit

$$\alpha_x \approx \exp(-Cx^{-b/2} - D) \tag{4b}$$

So, in a very early effort, Ito[15] on using this approximation found an expression for the dependence of $v_p$ on $v_0$ for $D = 0$. With the same approximation, we suceeded in deriving a complete closed solution for a polymerization system without chain transfer and termination exclusively by disproportionation.[14] Mahabadi, who had obtained similar results for this case,[16] tried to incorporate chain transfer and termination by combination into his reaction scheme. However, as he was not able to obtain a closed expression for the chain length distribution of dead polymer in the case of termination by recombination, he had to resort to a linearization of results obtained by numerical integration for several values of the parameter $b$. In the case of chain transfer, he was content with treating the limiting case of predominant chain transfer. On the other hand, in one of our previous communications,[11] we have applied a series development followed by an integration by terms in order to obtain the desired kinetic quantities for a kinetic scheme comprising chain transfer. Although this method is in principle successful except for a very narrow range of parameters, it is really satisfactory only in either of the two limiting ranges of predominant chain transfer or predominant termination where at most two or three terms suffice to describe the kinetic quantities with fair accuracy.

It is the primary aim of this work to overcome these deficiencies and to provide closed solutions (or at least reliable approximate solutions) for these very types of kinetic schemes, i.e., schemes including chain transfer and termination by chain recombination.

## II. Closed Expressions for the Integer Moments of the Chain Length Distribution of Dead Polymer Terminated by Recombination of Living Radicals

Usually, the integer moments $\mathbf{M}^{(i)}$ of the chain length distribution and their ratios (the various averages of the degree of polymerization as number average $\bar{P}_n$, weight average $\bar{P}_w$, and $z$ average $\bar{P}_z$) are calculated from the chain length distribution. Unfortunately, however, $n_2$, the chain length distribution of dead polymer terminated by recombination (and consisting of two independently grown chains, accordingly), which may be written ($n$ being the chain length distribution of living radicals)

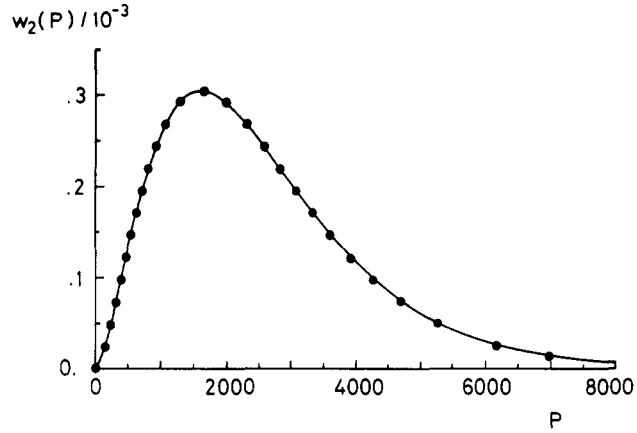


**Figure 1.** Weight distribution of chain lengths in dead polymer terminated by recombination $w_2(P) = Pn_2(P)/(\bar{P}_n)_2$ vs. degree of polymerization $P$ for $b = 0.16$ and $C = 0.002$ in the absence of chain transfer ($D = 0$): (—) approximate closed expression (calculated by using eq 20); (●) numerical result.[10]

$$n_2(P) \sim \int_1^{P-1} (P-p)^{-b/2} p^{-b/2} n(P-p) n(p)\, dp \sim \int_1^{P-1} (P-p)^{-b/2} p^{-b/2} \times \exp\left\{-\frac{2}{2-b} C[(P-p)^{(2-b)/2} + p^{(2-b)/2}]\right\} dp \tag{5}$$

as has been pointed out already earlier by various authors,[15,16] evades evaluation in closed form due to its nonintegrability. This is so even if the long-chain-limit expressions (evaluated by integration from 0 to $x$ in the exponent of eq 4b)

$$n(x) \sim \exp\left\{-\frac{2}{2-b} Cx^{(2-b)/2} - Dx\right\} \tag{6}$$

(here, of course with $D = 0$) are used for the distributions of living radicals $n(P)$ and $n(P-p)$ of length $p$ and $P-p$, respectively.

The integer moments of $n_2$ accordingly may be represented by

$$\mathbf{M}^{(i)} \sim \int_{P=2}^{\infty} p^i \left\{\int_{p=1}^{P-1} (P-p)^{-b/2} p^{-b/2} n(P-p) n(p)\, dp\right\} dP \tag{7}$$

As outlined in more generality and detail in the subsequent paper,[17] after reorganizing the double integral, this might be rewritten in terms of the variables $x$ and $y$ ($x + y = P$) to give

$$\mathbf{M}^{(i)} \sim \int_{x+y=2}^{\infty} (x+y)^i \left\{\int_{x=1}^{x+y-1} (xy)^{-b/2} n(x) n(y)\, dx\right\} d(x+y) \sim \int_{y=1}^{\infty} \int_{x=1}^{\infty} (x+y)^i (xy)^{-b/2} n(x) n(y)\, dx\, dy \tag{8}$$

On introducing the distribution of living chains $n(x)$ and $n(y)$ in the long-chain approximation (here for $D = 0$)

$$n(x) \sim \exp\{-C'x^{(2-b)/2}\} \tag{6a}$$

(with $C' = 2C/(2-b)$ for abbreviation) and, in accordance, shifting the lower limit of integration from unity down to zero, the evaluation of all terms appearing in eq 8 is straightforward due to their convenient factorizability, which is a direct consequence of the introduction of the

geometric mean approximation. Quite generally

$$\int_0^\infty \int_0^\infty x^m y^n x^{-b/2} y^{-b/2} e^{-C'x^{(2-b)/2}} e^{-C'y^{(2-b)/2}}\,dx\,dy = \left(\int_0^\infty x^{m-b/2} e^{-C'x^{(2-b)/2}}\,dx\right)\left(\int_0^\infty y^{n-b/2} e^{-C'y^{(2-b)/2}}\,dy\right) \equiv \mathbf{m}_m \cdot \mathbf{m}_n \tag{9}$$

with

$$\mathbf{m}_m = \frac{2}{2-b}(C')^{-(2m+2-b)/(2-b)}\Gamma\frac{2m+2-b}{2-b} \tag{10}$$

and $\mathbf{m}_n$ accordingly. Thus, the following expressions are obtained for the (relative) moments of $n_2(P)$:

$$\mathbf{M}^{(0)} \sim \mathbf{m}_0^2 = \left(\frac{2}{2-b}\right)^2 (C')^{-2} \tag{11a}$$

$$\mathbf{M}^{(1)} \sim 2\mathbf{m}_1\mathbf{m}_0 = 2\left(\frac{2}{2-b}\right)^2 (C')^{-(6-2b)/(2-b)}\Gamma\frac{4-b}{2-b} \tag{11b}$$

$$\mathbf{M}^{(2)} \sim 2\mathbf{m}_2\mathbf{m}_0 + 2\mathbf{m}_1^2 = 2\left(\frac{2}{2-b}\right)^2 (C')^{-(8-2b)/(2-b)}\left[\Gamma\frac{6-b}{2-b} + \left(\Gamma\frac{4-b}{2-b}\right)^2\right] \tag{11c}$$

$$\mathbf{M}^{(3)} \sim 2\mathbf{m}_3\mathbf{m}_0 + 6\mathbf{m}_2\mathbf{m}_1 = 2\left(\frac{2}{2-b}\right)^2 (C')^{-(10-2b)/(2-b)}\left[\Gamma\frac{8-b}{2-b} + 3\Gamma\frac{6-b}{2-b}\Gamma\frac{4-b}{2-b}\right] \tag{11d}$$

This leads to the following expressions for the various averages of the degree of polymerization of dead polymer terminated by recombination and, therefore, built up from *two* independently grown chains $(\bar{P})_2$:

$$(\bar{P}_n)_2 = \mathbf{M}^{(1)}/\mathbf{M}^{(0)} = 2(C')^{-2/(2-b)}\Gamma\frac{4-b}{2-b} \tag{12a}$$

$$(\bar{P}_w)_2 = \mathbf{M}^{(2)}/\mathbf{M}^{(1)} = (C')^{-2/(2-b)}\left[\left(\Gamma\frac{6-b}{2-b}\Big/\Gamma\frac{4-b}{2-b}\right) + \Gamma\frac{4-b}{2-b}\right] \tag{12b}$$

$$(\bar{P}_z)_2 = \mathbf{M}^{(3)}/\mathbf{M}^{(2)} = (C')^{-2/(2-b)}\frac{\Gamma\frac{8-b}{2-b} + 3\Gamma\frac{6-b}{2-b}\Gamma\frac{4-b}{2-b}}{\Gamma\frac{6-b}{2-b} + \left(\Gamma\frac{4-b}{2-b}\right)^2} \tag{12c}$$

with the polydispersity ratios

$$(\bar{P}_w/\bar{P}_n)_2 = \frac{1}{2} + \frac{1}{2}\Gamma\frac{6-b}{2-b}\Big/\left(\Gamma\frac{4-b}{2-b}\right)^2 \tag{13a}$$

$$(\bar{P}_z/\bar{P}_w)_2 = \Gamma\frac{4-b}{2-b}\,\frac{\Gamma\frac{8-b}{2-b} + 3\Gamma\frac{6-b}{2-b}\Gamma\frac{4-b}{2-b}}{\left(\Gamma\frac{6-b}{2-b} + \left(\Gamma\frac{4-b}{2-b}\right)^2\right)^2} \tag{13b}$$

As has been calculated earlier[14] the average degrees of polymerization of those chains terminated by disproportionation under the same conditions $(\bar{P})_1$, and therefore consisting of *one* independently grown chain only, are

$$(\bar{P}_n)_1 = (C')^{-2/(2-b)}\Gamma\frac{4-b}{2-b} \tag{14a}$$

$$(\bar{P}_w)_1 = (C')^{-2/(2-b)}\Gamma\frac{6-b}{2-b}\Big/\Gamma\frac{4-b}{2-b} \tag{14b}$$

$$(\bar{P}_z)_1 = (C')^{-2/(2-b)}\Gamma\frac{8-b}{2-b}\Big/\Gamma\frac{6-b}{2-b} \tag{14c}$$

As the same $\Gamma$ functions appear in eq 14 as in eq 12 and 13, the degrees of polymerization of polymer terminated by recombination may be easily expressed by those of polymer terminated by disproportionation. It follows

$$(\bar{P}_n)_2 = 2(\bar{P}_n)_1 \tag{15a}$$

$$(\bar{P}_w)_2 = (\bar{P}_w)_1 + (\bar{P}_n)_1 \tag{15b}$$

$$(\bar{P}_z)_2 = (\bar{P}_w)_1\frac{(\bar{P}_z)_1 + 3(\bar{P}_n)_1}{(\bar{P}_w)_1 + (\bar{P}_n)_1} \tag{15c}$$

and

$$(\bar{P}_w/\bar{P}_n)_2 = \frac{1}{2}(1 + (\bar{P}_w/\bar{P}_n)_1) \tag{16a}$$

$$(\bar{P}_z/\bar{P}_w)_2 = (\bar{P}_w)_1\frac{(\bar{P}_z)_1 + 3(\bar{P}_n)_1}{[(\bar{P}_w)_1 + (\bar{P}_n)_1]^2} \tag{16b}$$

## III. Evaluation of an Approximate Closed Form of the Chain Length Distribution of Dead Polymer Terminated by Recombination

Although the integer moments of a chain length distribution represent its most important properties and contain most of the desired information (and although the complete knowledge of all integer moments of a distribution in the strict sense is equivalent to the knowledge of the distribution), it might be profitable for some purposes to know the distribution itself, e.g., to analyze its form or to calculate moments other than the integer ones (as, for example, they are necessary to evaluate viscosity averages of the degree of polymerization of the polymer). As already mentioned in the preceding paragraph, this is not possible for the case of $n_2(P)$. However, in the following we shall try to derive an approximation for $n_2(P)$ that will be sufficiently accurate for nearly all purposes of practical interest.

The starting point is again eq 5. Making the substitution $p = P(v+1)/2$, considering the symmetric character of the function $f(v)$ to be integrated

$$\int_{-1}^{+1} f(v)\,dv = 2\int_0^1 f(v)\,dv$$

and introducing the long-chain approximation lead to

$$n_2(P) \sim P^{1-b}\int_0^1 (1-v^2)^{-b/2} \times \exp\left\{-\frac{2^{b/2}}{2-b}CP^{(2-b)/2}[(1+v)^{1-b/2} + (1-v)^{1-b/2}]\right\} dv \tag{17}$$

This is now approximated by separately averaging the preexponential factor $(1-v^2)^{-b/2}$

$$\int_0^1 (1-v^2)^{-b/2}\,dv = 2^{-b}\left(\Gamma\frac{2-b}{2}\right)^2/\Gamma(2-b) \tag{18}$$

and the expression within brackets in the exponent

$$\int_0^1 [(1+v)^{(2-b)/2} + (1-v)^{(2-b)/2}]\,dv = 2^{(6-b)/2}/(4-b) \tag{19}$$

yielding

$$n_2(P) \approx A^2P^{1-b}\frac{2-b}{2}\exp\{-AP^{(2-b)/2}\} \tag{20}$$

with $A = \{8/[(2-b)(4-b)]\}C$. This leads to the following

characteristic quantities for dead polymer terminated by recombination:

$$(\bar{P}_n)_2 = C^{-2/(2-b)}\left(\frac{8}{(2-b)(4-b)}\right)^{-2/(2-b)}\Gamma\frac{6-2b}{2-b}\Big/\Gamma\frac{4-2b}{2-b} \quad (21a)$$

$$(\bar{P}_w)_2 = C^{-2/(2-b)}\left(\frac{8}{(2-b)(4-b)}\right)^{-2/(2-b)}\Gamma\frac{8-2b}{2-b}\Big/\Gamma\frac{6-2b}{2-b} \quad (21b)$$

$$(\bar{P}_z)_2 = C^{-2/(2-b)}\left(\frac{8}{(2-b)(4-b)}\right)^{-2/(2-b)}\Gamma\frac{10-2b}{2-b}\Big/\Gamma\frac{8-2b}{2-b} \quad (21c)$$

$$(\bar{P}_\eta)_2 = C^{-2/(2-b)} \times \left(\frac{8}{(2-b)(4-b)}\right)^{-2/(2-b)}\left(\Gamma\frac{6-2b+2a}{2-b}\Big/\Gamma\frac{6-2b}{2-b}\right)^{1/a}$$

($a$ is the exponent in the limiting viscosity number–molecular weight relationship, $[\eta] = \text{const} \times \bar{M}^a$) as well as

$$(\bar{P}_w/\bar{P}_n)_2 = \Gamma\frac{8-2b}{2-b}\Gamma\frac{4-2b}{2-b}\Big/\left(\Gamma\frac{6-2b}{2-b}\right)^2 \quad (22a)$$

$$(\bar{P}_z/\bar{P}_w)_2 = \Gamma\frac{10-2b}{2-b}\Gamma\frac{6-2b}{2-b}\Big/\left(\Gamma\frac{8-2b}{2-b}\right)^2 \quad (22b)$$

## IV. Approximate Closed Treatment of a Kinetic Scheme Comprising Chain Transfer

When carrying out our numeric treatment of a reaction scheme with chain transfer and chain length dependent termination,[11] irrespective of whether the geometric or the harmonic mean approximation was applied, we observed power laws characterizing the relationships between rate of polymerization $v_p$ or degree of polymerization $\bar{P}_n$ (at constant chain-transfer agent concentration) and rate of initiation $v_0$ of the form

$$v_p \sim v_0^{\alpha} \quad (23)$$

$$\bar{P}_n \sim v_0^{-\beta} \quad (24)$$

which seemed to be valid over a wide range of initiation rates (several orders of magnitude) with exponents being intermediate between those of a "classical system" ($\alpha = 0.5$, $\beta = 0.5$) and those characteristic of a polymerization system with chain length dependent termination in the absence of chain transfer ($\alpha = (1-b)/(2-b)$, $\beta = 1/(2-b)$), the exact value of $\alpha$ and $\beta$ depending on the chain-transfer term $D$ (at a fixed range of $C$ values, i.e., initiation rates covered).

This finding points to the existence of a general way of translating the exponents $\alpha$ and $\beta$ in eq 23 and 24 into a (variable) exponent $k$ appearing in the expression characterizing the distribution of living chains $n(x)$ and vice versa which is not only valid for the limiting cases $D \gg C$ and $C \ll D$ but also for intermediate situations. If this argument were true, $n(x)$, which, in fact, is given by eq 6 in this case, could be alternatively expressed by

$$n(x) = \text{const} \times \exp(-Kx^k) \quad (25)$$

where $(2-b)/2 > k > 1$. Actually, a very careful inspection of eq 23 and 24 has revealed that the exponents $\alpha$ and $\beta$ are not really constant; i.e., the double-logarithmic plots according to these equations show a slight curvature, which, however, is so small that it will easily escape experimental or even visual detection. In view of that, we may approximate eq 6 by eq 25

$$n(x) = \text{const} \times \exp(-C'x^{(2-b)/2} - Dx) \approx \text{const} \times \exp(-Kx^k) \quad (25a)$$

hopefully expecting that the nearly negligible curvature in the double-logarithmic representations of eq 23 and 24, which is exhibited even if the rate of initiation is varied by a factor of $10^4$, will have its counterpart in a negligible curvature of a plot of ln $n(x)$ vs. $x^k$ with $k$ properly chosen. The replacement of the expression $C'x^{(2-b)/2} + Dx$, which constitutes a sum of two terms of (not greatly) different power in $x$, by an appropriately chosen single term of an intermediate power in $x$ has the most favorable effect that $n(x)$ in its approximate form, as will be shown below, can be processed to give a full outline of the kinetic expressions valid for the intermediate case ($C \approx D$). Actually, this goal could not be reached with the exact long-chain-limit form of $n(x)$ given by eq 6 due to its nonintegrability. In the following, we want to sketch the way of treating a polymerization system with chain length dependent termination and chain length independent chain transfer using eq 25 and comparing the results to those of our numerical treatment of the same system as well as to those obtained by the termwise integration of the expanded form of eq 6.[11]

**(1) Evaluation of the Parameters of Suitable Approximate Expressions for the Length Distribution of Living Chains in the Presence of Chain Transfer.** In principle, quite a number of ways may be adopted to assess the parameters $K$ and $k$ in the approximate expression for the length distribution of living chains $n(x)$ which is given by eq 25a. This might be accomplished by evaluating (a) the parameters of the tangent to the exact $n(x)$ given by eq 6 at a certain point $x = x_0$ or (b) the parameters of the straight line (secant) that can be drawn through two points at $x = x_0$ and $x = x_1$ of $n(x)$, eq 6. In case a we obtain

$$k = \frac{Cx_0^{-b/2} + D}{C'x_0^{-b/2} + D}$$

$$K = (C'x_0^{-b/2} + D)x_0^{1-k} \quad (26)$$

while for case b the result is

$$k = \ln\frac{C'x_1^{(2-b)/2} + Dx_1}{C'x_0^{(2-b)/2} + Dx_0}\Big/\ln\frac{x_1}{x_0}$$

$$K = (C'x_0^{-b/2} + D)x_0^{1-k} \quad (27)$$

Although the choice of $x_0$ (and $x_1$) is not very critical, it seems to be favorable to take $x_0$ (and eventually $x_1 > x_0$) from the region of chain lengths beyond the average chain length $\bar{x}$. A more detailed discussion of this subject is given in one of the following paragraphs.

A somewhat more elaborated approximate form for eq 6, which might replace eq 25 if an especially high degree of accuracy is desired, is presented in Appendix 1. In this development some allowance is made for the eventual slight deviation from linearity to be found in a double-logarithmic plot of eq 6, however, retaining the advantage of comfortable evaluability of the moments of distribution as for eq 25.

**(2) Evaluation of the Degrees of Polymerization Characteristic of a Polymerization System with Chain Transfer and Termination by Disproportionation as Mechanisms of Chain Radical Stabilization.** Once the distribution of living chains in the presence of chain transfer has a form that lends itself to the evaluation of its moments, the further procedure may follow the way

that has been outlined already earlier on treating a polymerization system without chain transfer and with termination by disproportionation.[10,14]

The $m$th moment of the (unnormalized) $x$ distribution, $n(x)$, eq 25, is given by

$$\mathbf{M}_x^{(m)} = \int_0^\infty x^m \exp(-Kx^k)\,dx = k^{-1}K^{-(m+1)/k}\Gamma\frac{m+1}{k} \tag{28}$$

This leads to the following expressions for the averages of living radical chain lengths:

$$\bar{x}_n = \mathbf{M}_x^{(1)}/\mathbf{M}_x^{(0)} = K^{-1/k}\frac{\Gamma(2/k)}{\Gamma(1/k)} \tag{29a}$$

$$\bar{x}_w = \mathbf{M}_x^{(2)}/\mathbf{M}_x^{(1)} = K^{-1/k}\frac{\Gamma(3/k)}{\Gamma(2/k)} \tag{29b}$$

$$\bar{x}_z = \mathbf{M}_x^{(3)}/\mathbf{M}_x^{(2)} = K^{-1/k}\frac{\Gamma(4/k)}{\Gamma(3/k)} \tag{29c}$$

The overall distribution of dead polymer (each polymer molecule here consisting of *one* independently grown chain only) is obtained by differentiation of eq 25 with respect to $x$

$$n_1(P) \approx KkP^{k-1}\exp(-KP^k) \tag{30}$$

where now $x$ has been formally replaced by $P$, the chain length of dead polymer. For the $m$th moment of $n_1(P)$, we obtain

$$\mathbf{M}_1^{(m)} = \int_0^\infty KkP^{m+k-1}\exp(-KP^k)\,dP = K^{-m/k}\Gamma\frac{m+k}{k} \tag{31}$$

These transform into the averages of the (overall) degree of polymerization

$$(\bar{P}_n)_1 \equiv \mathbf{M}_1^{(1)}/\mathbf{M}_1^{(0)} = K^{-1/k}\Gamma\frac{k+1}{k} \tag{32a}$$

$$(\bar{P}_w)_1 \equiv \mathbf{M}_1^{(2)}/\mathbf{M}_1^{(1)} = K^{-1/k}\frac{\Gamma(1+2/k)}{\Gamma(1+1/k)} = 2K^{-1/k}\Gamma(2/k)/\Gamma(1/k) = 2\bar{x}_n \tag{32b}$$

$$(\bar{P}_z)_1 \equiv \mathbf{M}_1^{(3)}/\mathbf{M}_1^{(2)} = K^{-1/k}\frac{\Gamma(1+3/k)}{\Gamma(1+2/k)} = 1.5K^{-1/k}\Gamma(3/k)/\Gamma(2/k) = 1.5\bar{x}_w \tag{32c}$$

**(3) Incorporation of Termination by Recombination.** If termination by disproportionation *and* recombination have to be considered as simultaneously occurring reactions, only the fraction

$$\delta = k_{t,dis}/(k_{t,dis} + k_{t,recomb}) \tag{33}$$

where $k_{t,dis}$ is the bimolecular rate constant of mutual termination by disproportionation and $k_{t,recomb}$ is the bimolecular rate constant of mutual termination by recombination, of all living radicals stabilized by termination will lead to the formation of polymer consisting of one independently grown chain. In the absence of chain transfer ($D = 0$), $\delta$ will also define the weight fraction of polymer terminated by disproportionation while its mole fraction $\epsilon$ is given by

$$\epsilon = 2k_{t,dis}/(2k_{t,dis} + k_{t,recomb}) = 2\delta/(1+\delta) \tag{33a}$$

Using the results contained in eq 15a–c, it is straightforward to formulate the various averages of the degree of polymerization for this situation

$$(\bar{P}_n)_{D=0} = \epsilon(\bar{P}_n)_1 + (1-\epsilon)(\bar{P}_n)_2 = (2-\epsilon)(\bar{P}_n)_1 = 2(\bar{P}_n)_1/(1+\delta) \tag{34a}$$

$$(\bar{P}_w)_{D=0} = \delta(\bar{P}_w)_1 + (1-\delta)(\bar{P}_w)_2 = (\bar{P}_w)_1 + (1-\delta)(\bar{P}_n)_1 \tag{34b}$$

$$(\bar{P}_z)_{D=0} = (\delta(\bar{P}_w)_1(\bar{P}_z)_1 + (1-\delta)(\bar{P}_w)_2(\bar{P}_z)_2)/(\bar{P}_w)_{D=0} = (\bar{P}_w)_1\frac{(\bar{P}_z)_1 + 3(1-\delta)(\bar{P}_n)_1}{(\bar{P}_w)_1 + (1-\delta)(\bar{P}_n)_1} \tag{34c}$$

where $(\bar{P}_n)_1$, $(\bar{P}_w)_1$, and $(\bar{P}_z)_1$ may be inserted from eq 14a–c.

The situation will be more complex if there is chain transfer *in addition* to termination by recombination (and disproportionation). In this case the general procedure outlined above in this section applies only to that fraction of the living chains which have been stabilized by termination. This quantity, however, is not directly available from our approximate distribution of living chains, eq 25, but might be obtained from the exact long-chain-limit form of $n(x)$, eq 6. Differentiation with respect to chain length $x$ gives the distribution of dead chains or—for that part which is subject to recombination on termination—of fragments of dead chains

$$dn(x)/dx \sim (Cx^{-b/2} + D)\exp(-C'x^{(2-b)/2} - Dx) \tag{35}$$

From eq 35 it is evident that for living chains stabilized after $x$ propagation steps, the fraction $\gamma = Cx^{-b/2}/(Cx^{-b/2} + D)$ will be stabilized by termination and the fraction $1 - \gamma = D/(Cx^{-b/2} + D)$ by chain transfer. For the same reasons as stated before for $n(x)$, it is not possible to obtain closed expressions for the moments of the chain length distributions of the two fractions of polymer, that stabilized by termination, and that by chain transfer. This difficulty, however, again may be overcome by substituting the approximate expression, eq 25a, for the exponential in eq 35.

$$n_1(P) \approx \text{const} \times (Cx^{-b/2} + D)\exp(-KP^k) \tag{36}$$

The expression for the distribution of living chains stabilized by chain transfer

$$n_{1,D}(P) \approx \text{const} \times D\exp(-KP^k) \tag{36a}$$

is identical with the distribution of living chains itself and, therefore, will give the same moments and averages, eq 29a–c. On the other side, the distribution of dead chains (or fragments to be recombined, respectively), will read

$$n_{1,C}(P) \approx \text{const} \times CP^{-b/2}\exp(-KP^k) \tag{36b}$$

with $K$ and $k$ defined by eq 26 or 27, and the constant being the same in eq 36a and 36b. For the $m$th moment of this latter distribution, we obtain

$$\mathbf{M}_C^{(m)} = \int_0^\infty P^{m-b/2}\exp(-KP^k)\,dP = k^{-1}K^{-(2+2m-b)/2k}\Gamma\frac{2+2m-b}{2k} \tag{37}$$

and for the averages

$$(\bar{T}_n)_1 = \mathbf{M}_C^{(1)}/\mathbf{M}_C^{(0)} = K^{-1/k}\frac{\Gamma((4-b)/2k)}{\Gamma((2-b)/2k)} \tag{38a}$$

$$(\bar{T}_w)_1 = \mathbf{M}_C^{(2)}/\mathbf{M}_C^{(1)} = K^{-1/k}\frac{\Gamma((6-b)/2k)}{\Gamma((4-b)/2k)} \tag{38b}$$

$$(\bar{T}_z)_1 = \mathbf{M}_C^{(3)}/\mathbf{M}_C^{(2)} = K^{-1/k}\frac{\Gamma((8-b)/2k)}{\Gamma((6-b)/2k)} \tag{38c}$$

In order to evaluate the average degrees of polymerization $(\bar{T})_2$ of those dead chains formed by recombination, which accordingly are built up of two independently grown

chains, the same principles may be used as put down in eq 15a–c

$$(\bar{T}_n)_2 = 2(\bar{T}_n)_1 \tag{39a}$$

$$(\bar{T}_w)_2 = (\bar{T}_w)_1 + (\bar{T}_n)_1 \tag{39b}$$

$$(\bar{T}_z)_2 = (\bar{T}_w)_1 \frac{(\bar{T}_z)_1 + 3(\bar{T}_n)_1}{(\bar{T}_w)_1 + (\bar{T}_n)_1} \tag{39c}$$

while for the overall degree of polymerization of that fraction of polymer which is stabilized by termination (disproportionation *and* recombination) in the presence of chain transfer, the formalism given by eq 34a–c can be used

$$\bar{T}_n = 2(\bar{T}_n)_1/(1 + \delta) \tag{40a}$$

$$\bar{T}_w = (\bar{T}_w)_1 + (1 - \delta)(\bar{T}_n)_1 \tag{40b}$$

$$\bar{T}_z = (\bar{T}_w)_1 \frac{(\bar{T}_z)_1 + 3(1 - \delta)(\bar{T}_n)_1}{(\bar{T}_w)_1 + (1 - \delta)(\bar{T}_n)_1} \tag{40c}$$

where all $\bar{T}$ are expressed by the corresponding averages $(\bar{T})_1$ of the uncoupled fragments subject to termination.

Finally, eq 29a–c and 40a–c may be combined by means of the procedure sketched in Appendix 2 to give the averages for the degree of polymerization of the overall *composite* polymer stabilized by termination (disproportionation and recombination) *and* chain transfer

$$(\bar{P}_n)_{composite} = (\tilde{C} + \tilde{D})((\tilde{C}/\bar{T}_n) + (\tilde{D}/\bar{x}_n))^{-1} \tag{41a}$$

$$(\bar{P}_w)_{composite} = (\tilde{C}\bar{T}_w + \tilde{D}\bar{x}_w)/(\tilde{C} + \tilde{D}) \tag{41b}$$

$$(P_z)_{composite} = \frac{\tilde{C}\bar{T}_w\bar{T}_z + \tilde{D}\bar{x}_w\bar{x}_z}{\tilde{C}\bar{T}_w + \tilde{D}\bar{x}_w} \tag{41c}$$

with $\tilde{C} = C\mathbf{M}_C^{(1)}$ and $\tilde{D} = D\mathbf{M}_x^{(1)}$ with all averages $x$ corresponding to transfer-stabilized polymer to be taken from eq 29a–c and those averages of termination-stabilized polymer $T$ to be traced back to eq 40a–c and further to eq 38a–c.

**(4) Effect of Chain Transfer on Rate of Polymerization, Kinetic Chain Length, and Apparent Rate Constant of Termination.** The presence of a chain-transfer agent naturally has the effect of shifting the average length of living polymer radicals to lower values. Although this has no consequences at all for the rate of polymerization $v_p$ (and all quantities related to it) in ideal classical free radical polymerization, the situation will be quite different if the termination constant depends on chain length as now the shortened living radicals will be subject to an increased probability of mutual termination since the termination constant increases with decreasing chain length. As a consequence, not only the rate of polymerization $v_p$ but also the kinetic chain length

$$\nu = v_p/v_0 \tag{42}$$

($v_0$ being the rate of initiation) and the apparent rate constant of mutual termination $\bar{k}_t$

$$\bar{k}_t = v_0/[R_{tot}]^2 \tag{43}$$

([$R_{tot}$] being the overall radical concentration) will be affected by addition of a chain-transfer agent to the polymerization system.

Once the moments of the distribution of living and dead (terminated by disproportionation) radicals in the presence of chain-transfer agents are available, it is straightforward to express $v_p$, $\nu$, and $\bar{k}_t$ through the appropriate moments also in the same general way as was done earlier in our numeric work.[11]

Actually, in the case of chain length dependent termination, the stationary overall radical concentration can be shown to differ from that of a "classical" polymerization by a factor $Q$

$$Q = \mathbf{M}_x^{(0)}/\mathbf{M}_C^{(0)} = \frac{\int_0^\infty \exp(-Kx^k)\,dx}{\int_0^\infty P^{-b/2}\exp(-KP^k)\,dP} = K^{-b/2k}\frac{\Gamma(1/k)}{\Gamma((2-b)/2k)} \tag{44}$$

As the rate of polymerization $v_p$ and the kinetic chain length each contain the overall radical concentration as a factor, they will be given accordingly by

$$v_p = (k_p^2/k_t^\circ)[M]^2CQ = (v_p)_0Q \tag{45}$$

and

$$\nu = C^{-1}Q = \nu_0Q \tag{42a}$$

while the apparent constant of termination, which contains the squared overall radical concentration in its denominator, may be represented by

$$\bar{k}_t = k_t^\circ Q^{-2} \tag{43a}$$

(The subscript zero index in eq 42a and 45 always refers to a polymerization system with a chain length independent termination constant $k_t^\circ$ at the same rate of initiation.)

Naturally, these relationships are not affected by the actual mechanism of termination (recombination or disproportionation).

## V. Discussion of Results from Approximate Closed Expressions and Comparison with Closed Expressions and Numeric Calculations

In principle, the check of the approximate closed expressions derived in the foregoing section may be carried out properly by comparing them either to closed expressions (where available) or to numeric results produced along the lines described in our earlier work.[9-11] It should be borne in mind, however, that all closed expressions (approximate *and* exact) are derived for the long-chain limit ($P,x \gg 1$) while the numeric data contain the genuine short-chain contributions. As a consequence, slight (relative) differences are bound to arise that will be of the order of $\bar{x}^{-1}$ or $\bar{P}^{-1}$ for degrees of polymerization.

**(a) Case of Termination by Recombination (without Chain Transfer).** Here an approximate closed expression (eq 20) has been derived for the chain length distribution of dead polymer. As no exact closed expression is available in this instance, comparison with only numeric data is possible. Figure 1 shows the result of such a comparison, carried out for the weight distribution, for $b = 0.16$ and $C = 0.002$. There is no indication whatsoever for any difference between the two distribution curves within the sensitivity of this plot.

A still more rigorous test of this approximate chain length distribution might be performed by comparing its moments (in the form of degrees of polymerization (eq 21a–c) and polydispersity ratios (eq 22a,b)) with the numeric results as well as the closed expressions (eq 12a–c and 13a,b, respectively). This is shown in Table I for several values of $b$ ranging from $b = 0.05$, which according to our Monte Carlo calculations approximately corresponds to the situation in Θ systems,[18] through $b = 0.16$ (the value characteristic of athermal systems[13]) up to $b = 0.25$ (the highest value of $b$ reported from experimental measure-

**Table I**
**Number-Average Degrees of Polymerization and Polydispersity Ratios of Dead Polymer Terminated by Recombination ($C = 0.0005$) in the Absence of Chain Transfer ($D = 0$)**

| | $(\bar{P}_n)_2$ | $(\bar{P}_n)_2/(\bar{P}_n)_1$ | $(\bar{P}_w/\bar{P}_n)_2$ | $(\bar{P}_z/\bar{P}_w)_2$ |
|---|---|---|---|---|
| $b = 0.05$ | | | | |
| exact[a] | 4788.77 | 2 | 1.52607 | 1.34774 |
| approx[b] | 4787.99 | 1.9997 | 1.52603 | 1.34771 |
| num[c] | 4791.05 | 2 | 1.52579 | 1.34767 |
| $b = 0.16$ | | | | |
| exact[a] | 7357.86 | 2 | 1.59200 | 1.38350 |
| approx[b] | 7344.54 | 1.9964 | 1.59155 | 1.38311 |
| num[c] | 7361.09 | 2 | 1.59166 | 1.38343 |
| $b = 0.25$ | | | | |
| exact[a] | 10873.4 | 2 | 1.65676 | 1.41781 |
| approx[b] | 10821.7 | 1.9905 | 1.65545 | 1.41667 |
| num[c] | 10878.0 | 2 | 1.65637 | 1.41772 |

[a] Calculated by using the exact eq 12, 13, and 15a. [b] Calculated by using approximate eq 21a–c, 22, and 14a. [c] Obtained by numeric procedures.

ments[5]). It is clear that the level of accuracy of the approximate results decreases a little with increasing value of the parameter $b$. Nevertheless, the agreement is still highly satisfactory even for $b = 0.25$. This might be most instructively extracted from the values for $(\bar{P}_n)_2/(\bar{P}_n)_1$, which deviate only negligibly from the exact (and trivial) value of 2 (see eq 15a) in the long-chain limit, at least up to $b = 0.25$. So even our approximate treatment shows a dramatic improvement over that provided by Mahabadi,[16] according to which the highly erroneous value of $(\bar{P}_n)_2/(\bar{P}_n)_1 = 2.143$ is obtained in this latter case.

It stands to reason that the data from the exact solution coincide perfectly with the numeric results if the latter are taken for high degrees of polymerization or, in the case of polydispersity ratios, are extrapolated to infinite chain length.

**(b) Case of Chain Transfer (in Addition to Termination). (i) Termination by Disproportionation.** Contrary to case a, it is no problem to formulate the ("exact") chain length distributions of living (eq 6) and dead (eq 35) polymer, the difficulty here being the evaluation of the moments of the distribution. As a consequence, we may, as a first step, check the adequacy of our

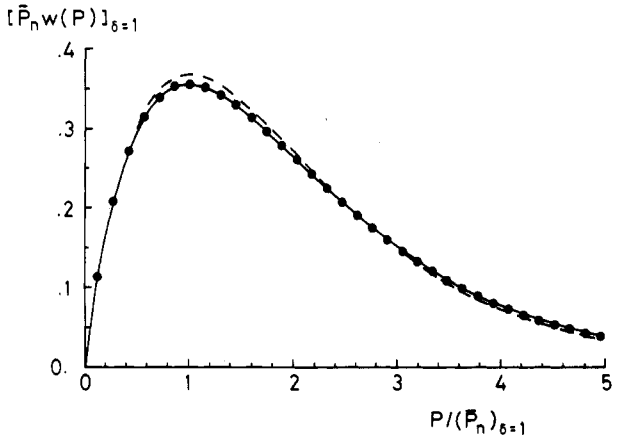


**Figure 2.** Normalized weight distribution of chain lengths in (composite) dead polymer terminated by disproportionation and chain transfer $[\bar{P}_n w(\bar{P})]_{\delta=1}$ vs. reduced degree of polymerization $P/(\bar{P}_n)_{\delta=1}$ for $b = 0.16$, $C = 0.001$, and $D = 0.001$: (—) approximate expression (obtained from eq 36); (●) exact expression (obtained from eq 35). Dashed line (– – –) is for $b = 0$.

(integrable) approximate distribution function, eq 36, which is to replace the exact one, eq 6, by a direct comparison. Deliberately choosing $x_0 = (C' + D)^{-1}$ and using, e.g., eq 26 for defining the parameters of our approximate distribution, we see that the graphical comparison given in Figure 2 does not show any resolvable differences between the exact and the approximate form.

As to the moments of the distribution, we have to resort to the results of the series expansion method[11] described previously as a reference or, where this method fails, to the results produced by a numeric integration of the "exact" distributions. On carrying out this more rigorous check, we find that the results are slightly dependent on the choice of the reference points $x_0$ and $x_1$. Table II for one specific point ($C = 0.0005$, $D = 0.0005$, $b = 0.16$) shows the influence of this choice, giving an impression of the differences that arise when either eq 26 or 27 is used in defining the parameters of our approximate distribution $k$ and $K$. Equally, Table II provides also an account of the increased accordance that may be achieved if the "improved" approximate form of the distribution developed in Appendix 1 is used.

**Table II**
**Test of the Accuracy of the Various Approximations Necessary for an Approximate Closed Treatment of a Polymerization System with Simultaneous Termination by Disproportionation ($C = 0.0005$) and Chain Transfer ($D = 0.0005$) at $b = 0.16$**

| $x_0(C' + D)$ | $x_1/x_0$ | $\bar{x}_n$ | $\bar{x}_w/\bar{x}_n$ | $\bar{x}_z/\bar{x}_w$ | $\bar{T}_n$ | $\bar{T}_w/\bar{T}_n$ | $\bar{T}_z/\bar{T}_w$ | $(\bar{P}_n)_1$ | $(\bar{P}_w/\bar{P}_n)_1$ | $(\bar{P}_z/\bar{P}_w)_1$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Exact Results Obtained by Termwise Integration[11] | | | | | | | | | | |
| | | 1293.9 | 2.0293 | 1.5142 | 1188.5 | 2.1189 | 1.5357 | 1254.6 | 2.0626 | 1.5220 |
| Tangent Method (Eq 26) | | | | | | | | | | |
| 1 | | 1296.5 | 2.0321 | 1.5160 | 1190.8 | 2.1219 | 1.5375 | 1255.7 | 2.0650 | 1.5241 |
| 2 | | 1294.6 | 2.0310 | 1.5154 | 1189.1 | 2.1207 | 1.5369 | 1255.2 | 2.0627 | 1.5232 |
| 3 | | 1293.9 | 2.0303 | 1.5151 | 1188.5 | 2.1199 | 1.5366 | 1255.4 | 2.0613 | 1.5228 |
| 5 | | 1293.5 | 2.0295 | 1.5147 | 1188.2 | 2.1191 | 1.5362 | 1256.0 | 2.0597 | 1.5221 |
| 10 | | 1293.8 | 2.0284 | 1.5142 | 1188.5 | 2.1179 | 1.5356 | 1257.6 | 2.0575 | 1.5213 |
| Secant Method (Eq 27) | | | | | | | | | | |
| 1 | 3 | 1294.6 | 2.0312 | 1.5156 | 1189.1 | 2.1209 | 1.5370 | 1255.0 | 2.0632 | 1.5234 |
| 2 | 1.5 | 1294.2 | 2.0307 | 1.5153 | 1188.7 | 2.1203 | 1.5367 | 1255.2 | 2.0620 | 1.5230 |
| 2 | 3 | 1293.4 | 2.0301 | 1.5150 | 1188.1 | 2.1197 | 1.5365 | 1255.2 | 2.0609 | 1.5226 |
| 2 | 6 | 1292.7 | 2.0296 | 1.5147 | 1187.5 | 2.1191 | 1.5362 | 1255.2 | 2.0598 | 1.5222 |
| 3 | 3 | 1293.2 | 2.0295 | 1.5147 | 1187.9 | 2.1190 | 1.5361 | 1255.8 | 2.0596 | 1.5221 |
| Improved Method (Appendix 1) | | | | | | | | | | |
| 1 | 3 | 1293.2 | 2.0278 | 1.5127 | 1188.0 | 2.1174 | 1.5341 | 1255.1 | 2.0608 | 1.5209 |
| 2 | 1.5 | 1293.8 | 2.0287 | 1.5137 | 1188.5 | 2.1183 | 1.5351 | 1255.8 | 2.0605 | 1.5215 |
| 2 | 3 | 1293.9 | 2.0290 | 1.5139 | 1188.5 | 2.1185 | 1.5353 | 1255.8 | 2.0607 | 1.5217 |
| 2 | 6 | 1294.0 | 2.0293 | 1.5142 | 1188.6 | 2.1189 | 1.5356 | 1255.7 | 2.0611 | 1.5220 |
| 3 | 3 | 1294.0 | 2.0290 | 1.5141 | 1188.7 | 2.1186 | 1.5356 | 1256.3 | 2.0601 | 1.5218 |

**Table III**
**Influence of Chain Transfer on Kinetic Data and Degrees of Polymerization for Various Extents of Chain Length Dependence of $k_t$ ($C$ = 0.0005)**

| | | | | living chains | | | disproportionation + transfer | | | recombination + transfer | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| code[a] | $D/10^{-4}$ | $\nu$ | $\bar{k}_t/k_t^\circ$ | $\bar{x}_n$ | $\bar{x}_w/\bar{x}_n$ | $\bar{x}_z/\bar{x}_w$ | $\bar{P}_n$ | $\bar{P}_w/\bar{P}_n$ | $\bar{P}_z/\bar{P}_w$ | $\bar{P}_n$ | $\bar{P}_w/\bar{P}_n$ | $\bar{P}_z/\bar{P}_w$ |
| $b$ = 0.05 | | | | | | | | | | | | |
| E | 0.0 | 2394.4 | 0.6977 | 2456.8 | 2.0258 | 1.5129 | 2394.4 | 2.0521 | 1.5194 | 4788.8 | 1.5261 | 1.3477 |
| E | 0.5 | 2387.4 | 0.7018 | 2182.2 | 2.0229 | 1.5114 | 2132.8 | 2.0464 | 1.5172 | 3854.6 | 1.6239 | 1.3700 |
| E | 2.5 | 2365.7 | 0.7148 | 1510.5 | 2.0159 | 1.5079 | 1486.5 | 2.0322 | 1.5119 | 2167.5 | 1.8165 | 1.4232 |
| E | 5.0 | 2346.7 | 0.7264 | 1092.4 | 2.0115 | 1.5057 | 1079.8 | 2.0234 | 1.5086 | 1402.4 | 1.9025 | 1.4535 |
| E | 10.0 | 2321.1 | 0.7424 | 704.22 | 2.0075 | 1.5037 | 698.90 | 2.0152 | 1.5056 | 822.77 | 1.9586 | 1.4775 |
| E | 50.0 | 2244.7 | 0.7939 | 184.01 | 2.0020 | 1.5010 | 183.64 | 2.0041 | 1.5015 | 191.47 | 1.9970 | 1.4980 |
| $b$ = 0.16 | | | | | | | | | | | | |
| E | 0.0 | 3678.9 | 0.2955 | 4017.4 | 2.0892 | 1.5442 | 3678.9 | 2.1840 | 1.5669 | 7357.9 | 1.5920 | 1.3835 |
| E | 0.5 | 3623.3 | 0.3047 | 3300.9 | 2.0730 | 1.5360 | 3067.6 | 2.1522 | 1.5548 | 5319.2 | 1.7160 | 1.4094 |
| T | | 3623.4 | 0.3047 | 3303.5 | 2.0745 | 1.5370 | 3069.8 | 2.1537 | 1.5558 | 5323.1 | 1.7169 | 1.4101 |
| I | | 3623.3 | 0.3047 | 3300.6 | 2.0725 | 1.5354 | 3067.3 | 2.1516 | 1.5542 | 5318.7 | 1.7157 | 1.4091 |
| E | 2.5 | 3476.3 | 0.3310 | 1945.4 | 2.0434 | 1.5211 | 1859.9 | 2.0919 | 1.5325 | 2539.2 | 1.8935 | 1.4572 |
| T | | 3476.4 | 0.3310 | 1947.1 | 2.0455 | 1.5226 | 1861.5 | 2.0941 | 1.5341 | 2541.3 | 1.8951 | 1.4583 |
| I | | 3476.4 | 0.3310 | 1945.3 | 2.0429 | 1.5206 | 1859.9 | 2.0914 | 1.5320 | 2539.1 | 1.8932 | 1.4568 |
| E | 5.0 | 3366.2 | 0.3530 | 1293.9 | 2.0293 | 1.5142 | 1254.6 | 2.0626 | 1.5220 | 1541.9 | 1.9504 | 1.4774 |
| T | | 3366.3 | 0.3530 | 1294.6 | 2.0310 | 1.5154 | 1255.3 | 2.0643 | 1.5232 | 1542.8 | 1.9518 | 1.4784 |
| I | | 3366.3 | 0.3530 | 1293.9 | 2.0290 | 1.5139 | 1254.6 | 2.0623 | 1.5217 | 1542.0 | 1.9501 | 1.4772 |
| E | 10.0 | 3233.3 | 0.3826 | 778.66 | 2.0181 | 1.5087 | 763.78 | 2.0390 | 1.5136 | 866.07 | 1.9810 | 1.4904 |
| T | | 3233.3 | 0.3826 | 778.87 | 2.0192 | 1.5096 | 763.98 | 2.0401 | 1.5144 | 866.30 | 1.9820 | 1.4911 |
| I | | 3233.4 | 0.3826 | 778.69 | 2.0179 | 1.5086 | 763.82 | 2.0388 | 1.5134 | 866.11 | 1.9809 | 1.4903 |
| E | 50.0 | 2887.1 | 0.4799 | 188.02 | 2.0048 | 1.5023 | 187.04 | 2.0105 | 1.5036 | 193.30 | 1.9989 | 1.4994 |
| T | | 2887.1 | 0.4799 | 188.03 | 2.0051 | 1.5026 | 187.05 | 2.0107 | 1.5039 | 193.31 | 1.9992 | 1.4996 |
| I | | 2887.1 | 0.4799 | 188.02 | 2.0048 | 1.5023 | 187.05 | 2.0104 | 1.5036 | 193.31 | 1.9989 | 1.4995 |
| $b$ = 0.25 | | | | | | | | | | | | |
| E | 0.0 | 5436.7 | 0.1353 | 6289.0 | 2.1489 | 1.5733 | 5436.7 | 2.3135 | 1.6116 | 10873.0 | 1.6568 | 1.4178 |
| E | 0.5 | 5244.1 | 0.1455 | 4643.6 | 2.1093 | 1.5531 | 4154.7 | 2.2354 | 1.5820 | 6880.2 | 1.7992 | 1.4433 |
| T | | 5245.8 | 0.1454 | 4664.1 | 2.1158 | 1.5572 | 4171.7 | 2.2423 | 1.5863 | 6908.1 | 1.8034 | 1.4462 |
| I | | 5243.7 | 0.1455 | 4636.6 | 2.1044 | 1.5478 | 4149.1 | 2.2304 | 1.5768 | 6871.0 | 1.7963 | 1.4400 |
| E | 2.5 | 4821.6 | 0.1721 | 2322.3 | 2.0561 | 1.5268 | 2186.3 | 2.1244 | 1.5421 | 2827.3 | 1.9428 | 1.4791 |
| T | | 4822.6 | 0.1720 | 2323.0 | 2.0625 | 1.5311 | 2193.2 | 2.1311 | 1.5465 | 2836.1 | 1.9479 | 1.4825 |
| I | | 4821.6 | 0.1721 | 2321.1 | 2.0538 | 1.5241 | 2185.3 | 2.1220 | 1.5394 | 2826.0 | 1.9410 | 1.4771 |
| E | 5.0 | 4548.9 | 0.1933 | 1445.6 | 2.0362 | 1.5172 | 1389.2 | 2.0812 | 1.5272 | 1639.6 | 1.9766 | 1.4905 |
| T | | 4549.3 | 0.1933 | 1448.1 | 2.0406 | 1.5202 | 1391.5 | 2.0856 | 1.5302 | 1642.3 | 1.9803 | 1.4930 |
| I | | 4549.0 | 0.1933 | 1445.4 | 2.0352 | 1.5160 | 1389.1 | 2.0801 | 1.5260 | 1639.4 | 1.9757 | 1.4896 |
| E | 10.0 | 4246.9 | 0.2218 | 829.44 | 2.0219 | 1.5103 | 809.41 | 2.0495 | 1.5164 | 894.67 | 1.9923 | 1.4967 |
| T | | 4247.0 | 0.2218 | 830.05 | 2.0244 | 1.5122 | 810.00 | 2.0520 | 1.5183 | 895.31 | 1.9946 | 1.4983 |
| I | | 4247.1 | 0.2218 | 829.47 | 2.0214 | 1.5099 | 809.45 | 2.0490 | 1.5160 | 894.71 | 1.9918 | 1.4963 |
| E | 50.0 | 3536.8 | 0.3198 | 190.58 | 2.0059 | 1.5028 | 189.30 | 2.0135 | 1.5045 | 194.50 | 2.0000 | 1.5000 |
| T | | 3536.8 | 0.3198 | 190.59 | 2.0065 | 1.5033 | 189.31 | 2.0141 | 1.5049 | 194.52 | 2.0006 | 1.5006 |
| I | | 3536.9 | 0.3198 | 190.58 | 2.0058 | 1.5027 | 189.30 | 2.0134 | 1.5044 | 194.51 | 2.0000 | 1.5000 |

[a] E = exact results obtained by series expansion,[11] T = results obtained by application of approximate expressions (parameters defined by eq 26) with $x_0 = 2/(C' + D)$, and I = results obtained by application of the "improved" approximate expressions (Appendix 1) (with $x_0 = 2/(C' + D)$ and $x_1 = 3x_0$).

From a careful study of the data given in Table II it might be concluded that there is practically no significant difference between the results produced by the "tangent" (eq 26) and the "secant" (eq 27) definition of the exponent $k$ if $x_0$ (or $x_0$ and $x_1$, respectively) refers to the same range of the distribution curve. As a general experience, it turns out to be profitable to take $x_0$ (and $x_1$) rather from the range of higher degrees of polymerization. While the quantities referring to living chains (eq 29), e.g., $x$, and those characteristic of the fraction of polymer that is terminated by disproportionation (eq 38), e.g., $T$, show nearly the same sensitivity toward the choice of reference points, the average degree of polymerization of the overall polymer $(\bar{P}_n)_1$, calculated from the differentiated approximate distribution (eq 30), and its polydispersity ratios (eq 32) are nearly independent of this choice, with the deviations from the reference values being small but practically constant. When the "improved" distribution curve is used (see Appendix 1), the choice of the reference points is still less important, as only extremely small variations occur when the points are changed. It is, however, interesting to note that the accuracy of the number-average degree of polymerization $(\bar{P}_n)_1$—and accordingly also of the ratio $(\bar{P}_w/\bar{P}_n)_1$—cannot be increased beyond a certain, albeit very high, level.

On the whole, however, the accordance of the results based on the (simple) approximate distribution curve (eq 25) with the "exact" results from the series expansion method is convincingly good for most of the applications of practical interest, especially if $x_0$ and (eventually) $x_1$ are chosen at $2(C' + D)^{-1}$ and $6(C' + D)^{-1}$, respectively. This is demonstrated in Table III, where a detailed comparison is carried out for the three most interesting values of $b$: $b$ = 0.05, $b$ = 0.16, and $b$ = 0.25. Clearly, the agreement again is better the smaller is the value of $b$ but even for high $b$ values, largely satisfactory results are obtained with the simple approximate distribution. (For $D$ = 0 and $b$ = 0.05 only a single value is given, as in the first case all approximations converge to the exact solution and in the second case the results obtained do not depend on the method applied for the number of places given.) The "improved" approximation leads to a better agreement in all cases, although a certain tendency for an overcorrection is to be noticed.

Table III now contains those overall degrees of polymerization that may be obtained alternatively by separately evaluating the data of the fractions of transfer-stabilized (i.e., living) and disproportionation-terminated polymer according to eq 40 and 41 with $\delta = 1$. These data invariably show a better agreement with the reference values than the values calculated from the differentiated distribution, eq 30 (which were the ones given in Table II). This might be due to the fact that eq 30 contains the decisive approximation in the preexponential *and* in the exponential term while the data derived from eq 41 refer to a distribution for which in fact only the latter is true. This general tendency is also observed for that polymer which is partly stabilized by chain transfer and partly by recombination (last three columns in Table III), the data of which are not accessible through the differentiated distribution eq 30 and can be obtained only by separate evaluation of the properties of the transfer-stabilized and the recombination-terminated polymer according to eq 40 and 41 with $\delta = 0$.

The general consequences which the simultaneous occurrence of chain transfer and of chain length dependent termination by disproportionation is bearing for the analysis of kinetic data have been described already in our numeric work.[11] They may be shortly summarized as follows:

(i) Mayo plots yield chain-transfer constants that are too high (fortunately the error does not exceed a few percent).

(ii) The apparent termination constant $\bar{k}_t$ characteristic of a polymerization experiment is nearly the same irrespective of whether the degree of polymerization of the polymer formed is controlled by disproportionation or by chain transfer (or a combination of both stabilization mechanisms).

(iii) There are slight but significant variations in the exponent relating the rate of polymerization to the rate of initiation, eq 23, in the presence of chain transfer agents.

Due to the extremely good agreement between the numerical results and those results derived from the approximate closed calculations, all these conclusions fully retain their validity and need no further discussion.

**(ii) Termination by Recombination.** As already mentioned in IV.3, eq 30 (and all further relations directly derived from it) no longer is able to give an adequate description of dead polymer properties if termination is at least partly by recombination. This is due to the fact that now part of the polymer consists of *two* independently grown chains. Naturally, these arguments are also pertinent to the chain length distribution of dead polymer for which, in addition to chain transfer, radical stabilization has been fully or partly by recombination.

Using the number fractions $\xi_{tr}$, $\xi_{dis}$, and $\xi_{recomb}$ of polymer stabilized by chain transfer, disproportionation, and recombination, respectively, developed in Appendix 2, we write overall composite chain length distribution $n_{composite}(P)$ as

$$n_{composite}(P) = \xi_{tr} n_{1,D}'(P) + \xi_{dis} n_{1,C}'(P) + \xi_{recomb} n_2'(P) \tag{46}$$

with $n_{1,D}'(P)$ and $n_{1,C}'(P)$ now being the *normalized* distributions of the contributions from chain transfer and disproportionation to be obtained by normalization from eq 36a and 36b. $n_2'(P)$, the normalized distribution of the dead polymer terminated by recombination, is approximately represented by

$$n_2'(P) \approx P^{1-b} \exp\left\{-\frac{2K}{k+1}P^k\right\}\left(\frac{2K}{k+1}\right)^{(2-b)/k} k/\Gamma\frac{2-b}{k} \tag{47}$$

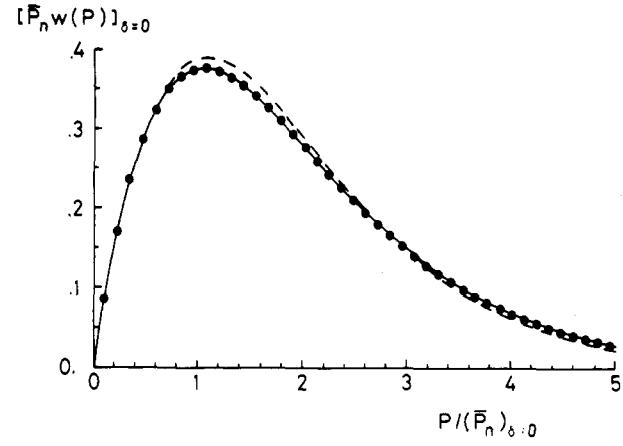


**Figure 3.** Normalized weight distribution of chain lengths in (composite) dead polymer terminated by recombination and chain transfer $[\bar{P}_n w(P)]_{\delta=0}$ vs. reduced degree of polymerization $P/(\bar{P}_n)_{\delta=0}$ for $b = 0.16$, $C = 0.001$, and $D = 0.001$: (—) approximate expression obtained from eq 46 with $\xi_{dis} = 0$, inserting eq 36a and 20 for $n_{1,D}(P)$ and $n_2(P)$, respectively; (●) exact expression obtained from eq 46 with $\xi_{dis} = 0$, inserting eq 6 and 5 for $n_{1,D}(P)$ and $n_2(P)$, respectively. Dashed line (– – –) is for $b = 0$.

This result is obtained when eq 5 is treated in the same way as outlined in section III, however, with the approximate distributions for living chains in the presence of chain transfer, eq 25, inserted for $n(P - p)$ and $n(p)$.

Figure 3 gives a comparison of the overall composite distribution $n_{composite}(P)$ for a polymer partly stabilized by chain transfer ($D = 0.001$) and by termination by recombination ($\delta = 0$, $C = 0.001$) for $b = 0.16$, calculated according to eq 46, with the corresponding distribution evaluated by iterative numeric procedures described earlier.[10,11] Again no differences are detectable even in this most complicated case. Table III in its last three columns shows the data referring to systems of this type evaluated by using eq 40 and 41. The agreement with the "exact" reference data calculated numerically in this even more serious test is practically perfect, especially if the "improved" approximate distribution (Appendix 1) is used.

It has already been mentioned that in case of $\delta = 1$ (termination exclusively by disproportionation), a practically unique relationship is obtained between the apparent rate constant of termination $\bar{k}_t$ and the degree of polymerization of the polymer formed irrespective of whether the variation of the degree of polymerization is accomplished by variation of the rate of initiation or by addition of a chain-transfer agent.[11] On a double-logarithmic plot of $\bar{k}_t/k_t°$ vs. $\bar{P}_n$ this relationship proved to be linear (not only for the geometric but also for the harmonic mean approximation), returning the exponent $b$ as the (negative) slope of this plot so that, quite generally, the following relationship is fulfilled:

$$\bar{k}_t/k_t° = \mathbf{A}\bar{P}^{-b} \tag{48}$$

where the numeric value of **A**, of course, depends on the type of average used for $\bar{P}$ ($\bar{P}_n$, $\bar{P}_w$, etc.) and also on the type of assumption used in assessing the influence of the length of the two radical chains $x$ and $y$ involved in the termination process (geometric mean assumption (eq 2) or harmonic mean assumption (eq 3)).

Once a reliable method is established to produce data of the kind given in the last three columns of Table III, it is straightforward to plot the relative apparent rate constant of termination $\bar{k}_t/k_t°$ vs. the number-average (or weight-average) degree of polymerization on a double-logarithmic scale also in this case in order to check whether the uniqueness of this $\bar{k}_t$–$\bar{P}_n$ plots is maintained if ter-

Table IV
Preexponential Factors $A_n$ and $A_w$ of the Power Laws $\bar{k}_t/k_t^\circ \sim \bar{P}_n^{-b}$ and $\bar{k}_t/k_t^\circ \sim \bar{P}_w^{-b}$, Respectively, for Various Values of $b$

| | $A_n$ | | | $A_w$ | | |
|---|---|---|---|---|---|---|
| $b$ | $D = 0$, $\delta = 0$, case a | $D = 0$, $\delta = 1$, case b | $D \gg C$, case c | $D = 0$, $\delta = 0$, case a | $D = 0$, $\delta = 1$, case b | $D \gg C$, case c |
| 0.05 | 1.0658 | 1.0295 | 1.0340 | 1.0886 | 1.0672 | 1.0667 |
| 0.10 | 1.1365 | 1.0604 | 1.0639 | 1.1877 | 1.1425 | 1.1403 |
| 0.16 | 1.2238 | 1.0993 | 1.1088 | 1.3231 | 1.2457 | 1.2389 |
| 0.20 | 1.2941 | 1.1265 | 1.1420 | 1.4250 | 1.3236 | 1.3118 |
| 0.25 | 1.3819 | 1.1620 | 1.1873 | 1.5678 | 1.4331 | 1.4120 |

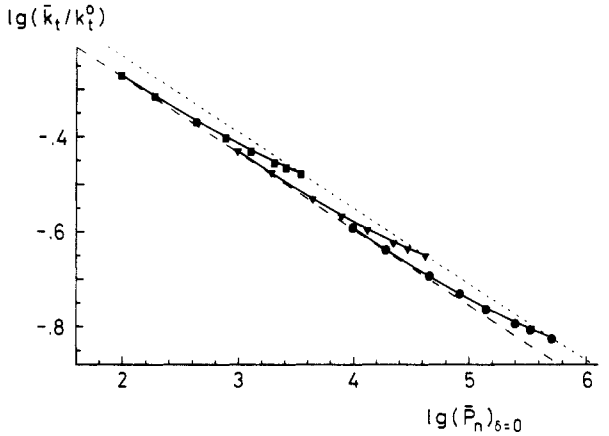


**Figure 4.** Double-logarithmic plots of $\bar{k}_t/k_t^\circ$ vs. degree of polymerization $(\bar{P}_n)_{\delta=0}$ in the case of stabilization by recombination and chain transfer for constant $C$ ((●) $C = 10^{-5}$; (▼) $C = 10^{-4}$; (■) $C = 10^{-3}$) and various values of $D$ (0, $C/10$, $C/5$, $C/2$, $C$, $2C$, $5C$, $10C$). The dotted line refers to a system without chain transfer ($D = 0$), and the broken line represents the limiting behavior for predominant chain transfer ($D \gg C$).

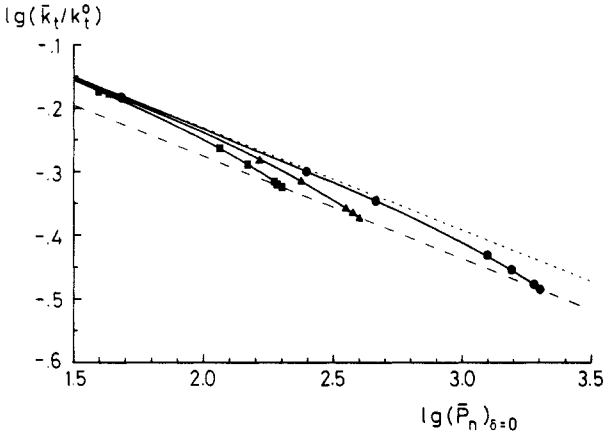


**Figure 5.** Double-logarithmic plots of $\bar{k}_t/k_t^\circ$ vs. degree of polymerization $(\bar{P}_n)_{\delta=0}$ in the case of stabilization by recombination and chain transfer for constant $D$ ((●) $D = 5 \times 10^{-4}$; (▼) $D = 25 \times 10^{-4}$; (■) $D = 50 \times 10^{-4}$) and various values of $C$ ($10^{-8}$, $10^{-4}$, $5 \times 10^{-4}$, $10^{-3}$, $5 \times 10^{-3}$, $10^{-2}$, $5 \times 10^{-2}$). The dotted line refers to a system without chain transfer ($D = 0$), and the broken line represents the limiting behavior for predominant chain transfer ($D \gg C$).

mination is no longer by disproportionation.

The resulting plots are given in Figure 4 (for varying $D$ and constant $C$; $C = 10^{-5}$, $C = 10^{-4}$, and $C = 10^{-3}$) and Figure 5 (varying $C$ and constant $D$; $D = 10.5 \times 10^{-3}$, $D = 2.5 \times 10^{-3}$, and $D = 5 \times 10^{-3}$). It is readily seen that in both cases the curves do not coincide, the points being spread over the space between the lower straight line characteristic of predominant chain transfer, $D \gg C$ (broken line), and the upper straight line referring to a system without chain transfer, $D = 0$, dotted line), both having a slope of $-b = -0.16$, which means that the second straight line, too, obeys the general law given by eq 48. In practice, the first type of plot (varying $D$ at constant $C$) gives an account of the increase of $\bar{k}_t$ on addition of chain-transfer agent, which is also responsible for the deviations from the classical Mayo plots to be observed even in polymerization systems with termination exclusively by disproportionation.[11] Here, however, as an additional complication, on increasing the transfer agent concentration, the formation of the (comparatively long chain) polymer molecules stabilized by recombination of two radicals is progressively repressed. This effect, which has long been known to be responsible for a many problems in the evaluation of chain-transfer constants even in classical free radical polymerization,[20] leads to a further decrease of the degree of polymerization, which makes the points tend toward the lower straight line with increasing transfer agent concentration.

The opposite effect is illustrated in the second, even more important case when, starting with a certain (usually ubiquitous) extent of chain-transfer activity, the rate of initiation is varied (Figure 5). Here increase in rate of initiation (termination) invariably leads to the progressive formation of recombined dead polymer molecules which consist of two independently grown chains and accordingly have about double the degree of polymerization of the transfer-stabilized molecules formed at the same rate of initiation. This leads to some compensation of the genuine reduction of the degree of polymerization taking place on increasing the rate of initiation and, as a consequence, makes the curves (constant $D$ and increasing $C$) tend from a point rather close to the lower straight line to one close to the upper one.

Due to this superposition of effects, the universality of the $\bar{k}_t$–$\bar{P}$ relationship is completely destroyed irrespective of whether the number- or weight-average degree of polymerization is taken. This breakdown is most clearly understandable on inspecting the numeric values (compiled in Table IV) which the constant $\mathbf{A}$ in eq 48 takes for the three most important limiting cases: (a) termination exclusively by recombination ($\delta = 0$) in the absence of chain transfer, (b) termination exclusively by disproportionation ($\delta = 1$) in the absence of chain transfer, and (c) predominance of chain transfer over termination as the mode of radical stabilization ($D \gg C$). $\mathbf{A} = \mathbf{A}_n$ if $\bar{P}_n$ is used in eq 48 and $\mathbf{A} = \mathbf{A}_w$ if $\bar{P}_w$ is used in eq 48. While $\mathbf{A}_n$ and $\mathbf{A}_w$ differ only slightly in the latter two cases (and probably will be indistinguishable experimentally), giving rise to the somewhat fortuitous universal behavior observed in the absence of termination by recombination ($\delta = 1$), $\mathbf{A}_n$ (and to a lesser extent also $\mathbf{A}_w$) differs appreciably for case a and c, even for moderate values of $b$. Plots of the type presented in Figures 4 and 5, which refer to a situation intermediate between the limiting cases a and c, therefore, no longer exhibit constant slopes if chain transfer *and* termination by recombination are simultaneously present in the polymerization system. With the standard proce-

dure[16] of taking the slope exhibited by the plot of experimental data as $-b$, plots of the type in Figure 4 formally will lead to $b$ values that are too low, while plots of the type given in Figure 5 (clearly the more important case) may give $b$ values that are much too high. As, on the one hand, some chain-transfer activity is inherent in any polymerization system and, on the other hand, as there is no way available to separate the two effects, extreme care has to be applied in the analysis of $\bar{k}_t$–$\bar{P}_n$ data in those systems where termination is partly or fully by recombination.

## VI. Conclusions

The methods and procedures developed herein allow one to obtain insight into the problems and complications that arise if chain transfer and termination by recombination of radicals are simultaneously present in a polymerization system exhibiting chain length dependent termination. The quantitative character of the relationships derived might give the key to experimentalists when trying for new techniques or when assessing suitable experimental conditions for successfully separating the influence of the various parameters involved.

## Appendix 1

As may be seen from the data collected in Tables II and III, the "tangent" method where the parameters $K$ and $k$ of eq 25 are defined by eq 26 yield results of fair accuracy for all important quantities. As eq 25 corresponds to a linear relationship between ln $n(x)$ and $x^k$, a further improvement might be achieved by taking account of the (slight) curvature exhibited by the "exact" eq 6 for $n(x)$.

Many standard methods in general may serve to reach this goal; however, we have to keep in mind that the "improved" form of $n(x)$ should be as tractable as the approximate form of eq 25. The following way turned out to be the simplest one fulfilling all the requirements.

We now mark all quantities referring to the new "improved" distribution with an asterisk and define the improved distribution $n^*(x)$ by

$$n^*(x) \sim [1 + B(x - x_0)^2] \exp(-Kx^k) \quad \text{(A1.1)}$$

where $x_0$ again is the point for which the parameters $K$ and $k$ have to be evaluated according to eq 26. The additional parameter $B$ is determined by forcing $n^*(x)$ through a second point at $x_1$, $n^*(x_1) = n(x_1)$, $n(x_1)$ being defined by eq 6. We obtain

$$B = (x_1 - x_0)^{-2}[\exp(Kx_1^k - C'x_1^{(2-b)/2} - Dx_1) - 1] \quad \text{(A1.2)}$$

Using the quantities $\mathbf{M}_x^{(m)}$ (eq 28), we may now represent the moments of the "improved" distribution of living chains by

$$\mathbf{M}^*{}_x^{(m)} = (1 + Bx_0^2)\mathbf{M}_x^{(m)} - 2Bx_0\mathbf{M}_x^{(m+1)} + B\mathbf{M}_x^{(m+2)} \quad \text{(A1.3)}$$

This distribution of dead polymer chains (stabilized by chain transfer or terminated by disproportionation) in analogy to eq 30 may be obtained by differentiating eq A1.1 with respect to $x$

$$n^*{}_1(P) = -\mathrm{d}n^*(x)/\mathrm{d}x = \exp(-KP^k)[KkP^{k-1}\{1 + B(P - x_0)^2\} - 2B(P - x_0)] \quad \text{(A1.4)}$$

Again the moments of this distribution may be written down in terms of those characterizing the old distribution (eq 30), $\mathbf{M}_1^{(m)}$, defined by eq 31, and that of the old distribution of living chains, $\mathbf{M}_x^{(m)}$ (eq 28)

$$\mathbf{M}^*{}_1^{(m)} = (1 + Bx_0^2)\mathbf{M}_1^{(m)} - 2Bx_0\mathbf{M}_1^{(m+1)} + B\mathbf{M}_1^{(m+2)} + 2Bx_0\mathbf{M}_x^{(m)} - 2B\mathbf{M}_x^{(m+1)} \quad \text{(A1.5)}$$

The alternative route is to build up $n^*{}_1(P)$ from the contributions of transfer-stabilized polymer $n^*{}_x(P)$, which is identical with the distribution of living chains, eq A1.1

$$n^*{}_D(P) = n^*(P) \sim [1 + B(x - x_0)^2] \exp(-Kx^k) \quad \text{(A1.6)}$$

and the contribution of disproportionation-terminated polymer

$$n^*{}_C(P) \sim x^{-b/2}[1 + B(x - x_0)^2] \exp(-Kx^k) \quad \text{(A1.7)}$$

according to

$$n^*(P) \sim [Cn^*{}_C(P) + Dn^*{}_D(P)] \quad \text{(A1.8)}$$

The moments of $n^*{}_C(P)$ may be expressed by those of the corresponding simple distribution eq 36b, $\mathbf{M}_C^{(m)}$, which are defined by eq 37

$$\mathbf{M}^*{}_C^{(m)} = (1 + Bx_0^2)\mathbf{M}_C^{(m)} - 2Bx_0\mathbf{M}_C^{(m+1)} + B\mathbf{M}_C^{(m+2)} \quad \text{(A1.9)}$$

Any moment of the overall composite distribution then is obtained by means of the mixing rule given in eq A1.8

$$(\mathbf{M}^{*(m)})_{\text{composite}} = C\mathbf{M}_C{}^{*(m)} + D\mathbf{M}_x{}^{*(m)} \quad \text{(A1.10)}$$

Ratios of the type $\mathbf{M}^{*(m+1)}/\mathbf{M}^{*(m)}$ then constitute the "improved" degrees of polymerization of living chains ($\mathbf{M}^*$ taken from eq A1.3 or "improved" degrees of polymerization of dead (transfer- and disproportionation-stabilized) polymer ($\mathbf{M}^*$ taken from either eq A1.5 or eq A1.10, respectively).

## Appendix 2

Quite generally, the following relationship holds true between the rate of chain transfer $v_{tr}$ and the rate of termination $v_t$

$$\frac{v_{tr}}{v_t} = \frac{k_{tr}[\mathrm{R_{tot}}][\mathrm{T}]}{k_t[\mathrm{R_{tot}}]^2} = \frac{k_{tr}[\mathrm{T}]}{k_t[\mathrm{R_{tot}}]} \quad \text{(A2.1)}$$

with $[\mathrm{R_{tot}}]$ being the overall stationary polymer radical concentration (see eq 43).

Dividing the numerator and the denominator of the right-hand side of eq A2.1 by $k_p[\mathrm{M}]$, the numerator yields the transfer term $D$ while the denominator represents the reciprocal kinetic chain length $\nu^{-1}$

$$\frac{v_{tr}}{v_t} = \frac{k_{tr}[\mathrm{T}]/(k_p[\mathrm{M}])}{k_t[\mathrm{R_{tot}}]/(k_p[\mathrm{M}])} = \frac{D}{\nu^{-1}} \quad \text{(A2.2)}$$

Substituting for $\nu$ from eq 42a and 44 finally defines $v_{tr}/v_t$ in terms of the parameters $C$ and $D$, which characterize the experimental conditions, and of the moments $\mathbf{M}_x^{(0)}$ and $\mathbf{M}_C^{(0)}$ taken from the distribution of living chains subject to stabilization by chain transfer and to stabilization by bimolecular termination, respectively (eq 44).

$$v_{tr}/v_t = D\mathbf{M}_x^{(0)}/(C\mathbf{M}_C^{(0)}) \quad \text{(A2.3)}$$

If termination is exclusively by disproportionation ($\delta = 1$), so that not only each transfer-stabilized polymer molecule but also each polymer molecule deactivated in bimolecular termination comprises one independently grown chain only, the ratio $v_{tr}/v_t$ also characterizes the number fractions $\xi_{dis}$ and $\xi_{tr}$ of transfer-stabilized and disproportionation-terminated chains in the polymer

$$(\xi_{dis})_{\delta=1} = C\mathbf{M}_C^{(0)}/(C\mathbf{M}_C^{(0)} + D\mathbf{M}_x^{(0)})$$
$$(\xi_{tr})_{\delta=1} = D\mathbf{M}_x^{(0)}/(C\mathbf{M}_C^{(0)} + D\mathbf{M}_x^{(0)}) \quad \text{(A2.4)}$$

If bimolecular termination is fully or partly by recombination ($\delta < 1$), the fraction of these polymer radicals subject to dimerization ($1 - \delta$) will decrease the number of dead polymer molecules originating from bimolecular

termination by a factor of $\delta + (1 - \delta)/2 = (1 + \delta)/2$.

This leads to the following expressions for the number fractions of disproportionation-terminated, recombination-terminated, and transfer-stabilized polymer molecules, $\xi_{dis}$, $\xi_{recomb}$, and $\xi_{tr}$, respectively:

$$\xi_{dis} = 2\delta C\mathbf{M}_C^{(0)}/[(1 + \delta)C\mathbf{M}_C^{(0)} + 2D\mathbf{M}_x^{(0)}]$$

$$\xi_{recomb} = (1 - \delta)C\mathbf{M}_C^{(0)}/[(1 + \delta)C\mathbf{M}_C^{(0)} + 2D\mathbf{M}_x^{(0)}]$$

$$\xi_{tr} = 2D\mathbf{M}_x^{(0)}/[(1 + \delta)C\mathbf{M}_C^{(0)} + 2D\mathbf{M}_x^{(0)}] \quad \text{(A2.5)}$$

Weight fractions $\omega$ may be evaluated by taking into account the individual (number) average degrees of polymerization of each contribution, i.e., $(\bar{P}_n)_1$ (eq 38a), $(\bar{P}_n)_2$ (eq 39a), and $\bar{x}_n$ (eq 29a) for the parts stabilized by disproportionation, recombination, and chain transfer, respectively:

$$\omega_{dis} = \delta C\mathbf{M}_C^{(1)}/(C\mathbf{M}_C^{(1)} + D\mathbf{M}_x^{(1)})$$

$$\omega_{recomb} = (1 - \delta)C\mathbf{M}_C^{(1)}/(C\mathbf{M}_C^{(1)} + D\mathbf{M}_x^{(1)})$$

$$\omega_{tr} = D\mathbf{M}_x^{(1)}/(C\mathbf{M}_C^{(1)} + D\mathbf{M}_x^{(1)}) \quad \text{(A2.6)}$$

Standard summation procedures lead to the various averages of the degree of polymerization of the overall composite polymer

$$(\bar{P}_n)_{composite} = (\sum_i \omega_i/(\bar{P}_n)_i)^{-1}$$

$$(\bar{P}_w)_{composite} = \sum_i \omega_i(\bar{P}_w)_i$$

$$(\bar{P}_z)_{composite} = \sum_i \omega_i(\bar{P}_w\bar{P}_z)_i/(\sum_i \omega_i(\bar{P}_w)_i) \quad \text{(A2.7)}$$

## References and Notes


(1) Schulz, G. V. *Z. Phys. Chem.* **1956**, *8*, 284.
(2) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1959**, *81*, 1339.
(3) North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859.
(4) Allen, P. E.; Patrick, C. R. *Makromol. Chem.* **1961**, *47*, 154; **1964**, *72*, 106.
(5) O'Driscoll, K. F.; Mahabadi, H. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 869. Mahabadi, H. K.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1977**, *11*, 967.
(6) Yasukawa, T.; Murakami, K. *Polymer* **1980**, *21*, 1423; *Macromolecules* **1981**, *14*, 227.
(7) Kamachi, M. *Makromol. Chem., Suppl.* **1985**, *14*, 17.
(8) Kamachi, M.; Ninomiya, S.; Nozakura, S.; Yasukawa, T.; Murakami, K. *Polym. Prep. Jpn.* **1982**, *31*, 133.
(9) Olaj, O. F.; Zifferer, G.; Gleixner, G. Preprints of "Makromolekulares Kolloquium", Freiburg/Brsg., Germany, March 4–6, 1982, pp 21–22; see also: Zifferer, G. Doctoral Thesis, University of Vienna, 1982.
(10) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem.* **1986**, *187*, 977.
(11) Olaj, O. F.; Zifferer, G.; Gleixner, G.; Stickler, M. *Eur. Polym. J.* **1986**, *22*, 585.
(12) Khokhlov, A. R. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 633.
(13) Olaj, O. F.; Zifferer, G. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 549.
(14) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 773, 851.
(15) Ito, K., *J. Polym. Sci., Part A-2* **1969**, *7*, 241; *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1991.
(16) Mahabadi, H. K. *Macromolecules* **1985**, *18*, 1319.
(17) Olaj, O. F.; Zifferer, G. *Macromolecules*, following paper in this issue.
(18) Olaj, O. F.; Zifferer, G. Preprints of the 28th IUPAC Macromolecular Symposium, Amherst, MA, July 12–16, 1982, p 511.
(19) As an example, the local apparent exponent $\alpha$ in eq 23 relating the rate of polymerization $v_p$ to the rate of initiation $v_0$ for a system with $b = 0.16$ in the presence of chain transfer ($D = 0.0005$) varies from 0.4912 at $C = 0.00025$ through 0.4852 (at $C = 0.0005$) to 0.4776 at $C = 0.001$. It is interesting to note that, for the number of places given, these results, which are obtained by differentiation of the approximate expressions as listed in Table II, not only are independent of the choice of the method but also agree perfectly with the exact values evaluated numerically.
(20) Henrici-Olivé, G.; Olivé, S. *Adv. Polym. Sci.* **1961**, *2*, 496.


# Termination Processes in Free Radical Polymerization. 9. Derivation of Universal Relationships between Kinetic Quantities for Arbitrary Chain Length Dependence of the Termination Constant†


**Oskar Friedrich Olaj* and Gerhard Zifferer**

*Institute of Physical Chemistry, University of Vienna, A-1090 Vienna, Austria.*

*Received June 12, 1986*


ABSTRACT: Without reference to any special type of the dependence of the rate constant of bimolecular termination $k_t(x,y)$ on the chain lengths ($x$ and $y$) of the two radicals involved, universal relations are derived between the basic quantities characteristic of the polymerization kinetics of such a system. When $k_t(x,y)$ can be factorized, simple expressions may be obtained also if termination is by recombination. These universal relationships have been successfully tested for a power law dependence of $k_t$ on various means $\overline{x,y}$, $k_t = k_t^\circ(\overline{x,y})^{-b}$. Their use provides comfortable access to resolving the kinetic scheme. Thus, for the geometric mean in its long-chain approximation, $k_t = k_t^\circ(xy)^{-b/2}$, a complete resolution of the kinetic scheme free from any further assumptions could be worked out. In addition, the numeric results obtained for various means $\overline{x,y}$ are discussed and analyzed with respect to the possibility of obtaining experimental information on which type of mean $\overline{x,y}$ is operative in the bimolecular termination process of free radical polymerization.


## I. Introduction

During the past years progressively increasing interest has been devoted to the problem of the chain length dependence of the termination rate constant $k_t$ in free radical polymerization with reference to both its experimental verification and its adequate theoretical treatment (see ref 1 and literature cited therein).

Although only very simple specific forms of such a dependence of $k_t$ on the chain lengths $x$ and $y$ of the two radical chains involved in the termination process

$$k_t(x,y) = k_t^\circ F(x,y) \quad (1)$$

have been used in calculations so far[1-7] (in fact, only results for the geometric mean approximation

† Affectionately dedicated to Prof. Dr. K. L. Komarek, Institute of Inorganic Chemistry, University of Vienna, on occasion of his 60th birthday, together with our best wishes.

0024-9297/87/2220-0850$01.50/0 