Macromolecules **1987**, *20*, 850–861

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, ξ_{dis}, ξ_{recomb}, and ξ_{tr}, respectively:

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

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

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

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

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

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

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

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

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

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

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

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 α 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

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

and for the harmonic mean approximation

$$F(x,y) = (2xy/(x+y))^{-b} \qquad (3)$$

have been reported to date), the results have invariably shown that we have to part with nearly all the familiar relationships that over the decades have been established for the so-called "classical" free radical polymerization with chain length independent termination.

On the other hand, however, the closed solutions that are available for the geometric mean assumption,[1-4,6] eq 2, have revealed the occasional existence of regularities.[6] So, for instance, it turned out that the (second) polydispersity ratio $\bar{P}_z/\bar{P}_w$ of dead polymer terminated by disproportionation in the absence of chain transfer was in a simple relationship to the (first) polydispersity ratio of living chains $\bar{x}_w/\bar{x}_n$, $\bar{P}_z/\bar{P}_w = 3\bar{x}_w/4\bar{x}_n$. This proved to be of general validity as it could be confirmed also for the numerical results obtained with the geometric and the harmonic mean approximation for long chains. As some further hints for the existence of such regularities also could be derived from our numeric treatment of polymerization systems including chain transfer,[7] there seems to be some hope that there might be a quite general set of characteristic relationships that defines the interdependence of all the important quantities appearing in the kinetic scheme irrespective of the specific form of the chain length dependence $F(x,y)$ of the termination constant and that contains the solutions of the classical polymerization scheme as a degenerate case.

In the following sections we set out to derive these relationships and try to show how these may be used in obtaining general solutions of the kinetic scheme.

II. Development of Universal Relationships

A. Preliminaries. The subject of our considerations is—as in our recent communications[1,7]—a kinetic scheme comprising the reactions radical formation from initiator I,

$$\mathrm{I} \rightarrow 2\mathrm{R}_0; \qquad \text{rate } v_0 \qquad (4)$$

chain propagation,

$$\mathrm{R}_x + \mathrm{M} \rightarrow \mathrm{R}_{x+1}$$

$$v_p = k_p[\mathrm{M}]\sum_x[\mathrm{R}_x] \qquad (5)$$

chain length dependent termination,

$$\mathrm{R}_x + \mathrm{R}_y \rightarrow \mathrm{P}$$

$$v_t = \sum_x\sum_y k_t(x,y)[\mathrm{R}_x][\mathrm{R}_y] = k_t^\circ\sum_x\sum_y F(x,y)[\mathrm{R}_x][\mathrm{R}_y] \qquad (6)$$

and chain transfer to some chain-transfer agent T (which also may be monomer).

$$\mathrm{R}_x + \mathrm{T} \rightarrow \mathrm{P} + \mathrm{R}_0$$

$$v_{tr} = k_{tr}[\mathrm{T}]\sum_x \mathrm{R}_x \qquad (7)$$

The last reaction is assumed to yield—besides transfer-stabilized polymer—transfer radicals that are not distinguished from the primary radicals formed by decay of initiator: both types of radicals of "zero degree of polymerization" contribute to $[\mathrm{R}_0]$ and are postulated to react quantitatively with monomer with the rate constant of regular chain propagation k_p without undergoing any termination. This assessment ensures that the fraction of $[\mathrm{R}_0]$ that originates from the initiator is not susceptible to an eventual chain length dependence of k_t without doing much harm to the realism of the scheme.

The basic quantity to start with again is the propagation probability α_x, which not only defines the fraction of chain radicals of length x, R_x, being transformed into chain radicals of length x+1, R_{x+1}, by chain propagation but also relates the stationary concentrations of chain radicals of adjacent chain lengths

$$\alpha_x = [\mathrm{R}_x]/[\mathrm{R}_{x-1}] = \left(1 + \frac{k_{tr}[\mathrm{T}]}{k_p[\mathrm{M}]} + \frac{k_t^\circ}{k_p[\mathrm{M}]}\sum_y F(x,y)[\mathrm{R}_y]\right)^{-1} \qquad (8)$$

This latter fact allows us to trace back all the stationary radical concentrations $[\mathrm{R}_x]$ and $[\mathrm{R}_y]$, respectively, to $[\mathrm{R}_0]$ according to

$$[\mathrm{R}_x] = [\mathrm{R}_0]\prod_{i=1}^{x}\alpha_i$$

$$[\mathrm{R}_y] = [\mathrm{R}_0]\prod_{j=1}^{y}\alpha_j \qquad (9)$$

The expressions for rate of propagation v_p, rate of termination v_t, and rate of chain transfer v_{tr} accordingly take the forms

$$v_p = k_p[\mathrm{M}][\mathrm{R}_0]\sum_x\prod_{i=1}^{x}\alpha_i \qquad (5a)$$

$$v_t = k_t^\circ[\mathrm{R}_0]^2\sum_x\sum_y F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (6a)$$

$$v_{tr} = k_{tr}[\mathrm{T}][\mathrm{R}_0]\sum_x\prod_{i=1}^{x}\alpha_i \qquad (7a)$$

We note that two types of sums appear in the kinetic scheme: those explicitly containing the function $F(x,y)$ characterizing the chain length dependence of termination (eq 6a) and those referring to the overall concentration of radicals (eq 5a and 7a), which are only indirectly influenced by $F(x,y)$ as $F(x,y)$, of course, enters also into the expression for α_x, eq 8.

Using symmetry arguments regarding x and y, we may consider the double sum contained in eq 7a, for convenience, to be equivalent to a squared single sum, which we denote by S_1

$$S_1^2 \equiv \sum_x\sum_y F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (10)$$

On the other hand, we denote the sum contained in eq 5a and 7a by S_2

$$S_2 \equiv \sum_x\prod_{i=1}^{x}\alpha_i \qquad (11)$$

The kinetic chain length ν then is given by

$$\nu = v_p/v_t = \frac{k_p[\mathrm{R}_0][\mathrm{M}]S_2}{k_t^\circ[\mathrm{R}_0]^2S_1^2} = \frac{k_p[\mathrm{M}]}{k_t^\circ[\mathrm{R}_0]S_1}\,\frac{S_2}{S_1} \qquad (12)$$

On recalling that the (eventual) difference between S_2 and S_1, which is caused by $F(x,y)$, obviously will vanish in the case of "classical" free radical polymerization, for which $F(x,y) = 1$ for any x and y, we find that the meaning of the factor $k_p[\mathrm{M}]/k_t^\circ[\mathrm{R}_0]S_1$ becomes clear at once: It constitutes the kinetic chain length $\nu_0 \equiv C^{-1}$ that would be obtained under the same conditions of initiation; however, in the case of chain length independent termination

$$\nu_0 = \frac{k_p[\mathrm{M}]}{k_t^\circ[\mathrm{R}_0]S_1} = \frac{1}{C} \qquad (13)$$

Therefore the quantities ν_0 and C, respectively, depend on the rate of initiation only and accordingly can be taken as a measure of v_0.

Now, on denoting the so-called transfer term $k_{tr}[T]/(k_p[M])$ appearing in eq 8 by D, substituting for $[R_y]$ from eq 9, and introducing eq 13, we may rewrite the expression for α given by eq 8 in the form

$$\alpha_x = (1 + D + (C/S_1)\sum_y F(x,y)\prod_{j=1}^{y}\alpha_j)^{-1} \qquad (8a)$$

Eliminating $\sum_y F(x,y)\prod_{j=1}^{y}\alpha_j$ between eq 8a and 10 finally allows us to write down a formal expression for S_1

$$S_1 = C^{-1}\sum_{x=1}^{\infty}(\alpha_x^{-1} - D - 1)\prod_{i=1}^{x}\alpha_i \qquad (14)$$

On the one hand, this has the effect of removing the explicit dependence of S_1 on y (S_1 now depends only indirectly on y via α_x) and reducing the quadratic form of S_1 defined by eq 10 to a first degree expression on the other.

S_1 (eq 14) as well as S_2 (eq 11) can be understood as (zeroth) moments of the distributions

$$f_1(x) = C^{-1}(\alpha_x^{-1} - D - 1)\prod_{i=1}^{x}\alpha_i \qquad (15)$$

and

$$f_2(x) = \prod_{i=1}^{x}\alpha_i \qquad (16)$$

respectively. While $f_2(x)$ is at once recognized to be the (unnormalized) length distribution of living chains and therefore has the meaning of $n(x)$ of our preceding paper,[1] it takes eq 8a followed by some rearrangement to show that $f_1(x)$ is the (unnormalized) length distribution of dead chains stabilized by bimolecular termination through disproportionation or, more generally, the length distribution of such chain fragments if termination is not exclusively by disproportionation but also by recombination. As a consequence, $f_1(x)$ is equivalent to $n_{1,C}$ of our previous paper.[1]

The general moments $S_1^{(k)}$ and $S_2^{(k)}$, therefore, are formulated as

$$S_1^{(k)} = C^{-1}\sum_{x=1}^{\infty}x^k(\alpha_x^{-1} - D - 1)\prod_{i=1}^{x}\alpha_i \qquad (17a)$$

or alternatively, in terms of the original definition of S_1, eq 10

$$S_1^{(k)} = (1/S_1^{(0)})\sum_x x^k\sum_y F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (17b)$$

and

$$S_2^{(k)} = \sum_{x=1}^{\infty}x^k\prod_{i=1}^{x}\alpha_i \qquad (18)$$

from which the various averages $\bar{T}$ and $\bar{x}$ of the degree of polymerization of disproportionation-terminated polymer ($\bar{T} = S_1^{(k+1)}/S_1^{(k)}$) and of living (or transfer-stabilized) polymer ($\bar{x} = S_2^{(k+1)}/S_2^{(k)}$), respectively, may be easily formulated ($k = 0$: number average; $k = 1$: weight average; $k = 2$: z average).

B. General Relationships between $S_1^{(k)}$ and $S_2^{(k)}$. Using eq 8a, we write the distribution of dead polymer (if termination is by disproportionation only) or of the independently grown fragments contained in dead polymer (if there is also termination by recombination) as

$$n_1(P) \equiv (1 - \alpha_P)\prod_{i=1}^{P-1}\alpha_i = [D + (C/S_1^{(0)})\sum_{y=1}^{\infty}F(P,y)\prod_{j=1}^{y}\alpha_j]\prod_{i=1}^{P}\alpha_i \qquad (19)$$

This yields the following expression for its moments $S_3^{(k)}$:

$$S_3^{(k)} \equiv \sum P^k n_1(P) = D\sum P^k\prod_{i=1}^{P}\alpha_i + (C/S_1)\sum_P\sum_y F(P,y)P^k\prod_{i=1}^{P}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (20a)$$

which by means of eq 17b and 18 transforms into the important general relationship

$$S_3^{(k)} = CS_1^{(k)} + DS_2^{(k)} \qquad (20b)$$

which immediately allows us to express the various averages of the degree of polymerization of uncoupled dead polymer $S_3^{(k+1)}/S_3^{(k)}$ in terms of $S_1^{(k)}$ and $S_2^{(k)}$.

On the other hand, $S_3^{(k)}$ may be evaluated alternatively by inserting the expressions developed for $S_1^{(k)}$ and $S_2^{(k)}$ in the previous paragraph, eq 17 and 18, into eq 20b

$$CS_1^{(k)} + DS_2^{(k)} = \sum_{x=1}^{\infty}x^k(\alpha_x^{-1} - D - 1)\prod_{i=1}^{x}\alpha_i + D\sum_{x=1}^{\infty}x^k\prod_{i=1}^{x}\alpha_i = \sum_{x=1}^{\infty}x^k\prod_{i=1}^{x-1}\alpha_i - \sum_{x=1}^{\infty}x^k\prod_{i=1}^{x}\alpha_i = 1^k + \alpha_1(2^k - 1^k) + \alpha_1\alpha_2(3^k - 2^k) + \alpha_1\alpha_2\alpha_3(4^k - 3^k) + ... \qquad (21)$$

This leads to the following equations:

$$k = 0:\ CS_1^{(0)} + DS_2^{(0)} = 1 \qquad (22a)$$

$$k = 1:\ CS_1^{(1)} + DS_2^{(1)} = 1 + S_2^{(0)} \qquad (22b)$$

$$k = 2:\ CS_1^{(2)} + DS_2^{(2)} = 1 + S_2^{(0)} + 2S_2^{(1)} \qquad (22c)$$

$$k = 3:\ CS_1^{(3)} + DS_2^{(3)} = 1 + S_2^{(0)} + 3S_2^{(1)} + 3S_2^{(2)} \qquad (22d)$$

Equating the expressions referring to identical quantities, we finally obtain

$$S_3^{(0)} = CS_1^{(0)} + DS_2^{(0)} = 1 \qquad (23a)$$

$$S_3^{(1)} = CS_1^{(1)} + DS_2^{(1)} = \bar{P}_n = 1 + S_2^{(0)} \qquad (23b)$$

$$S_3^{(2)} = CS_1^{(2)} + DS_2^{(2)} = \bar{P}_n\bar{P}_w = 1 + S_2^{(0)} + 2S_2^{(1)} \qquad (23c)$$

$$S_3^{(3)} = CS_1^{(3)} + DS_2^{(3)} = \bar{P}_n\bar{P}_w\bar{P}_z = 1 + S_2^{(0)} + 3S_2^{(1)} + 3S_2^{(2)} \qquad (23d)$$

and consequently

$$\bar{P}_n = 1 + S_2^{(0)} \qquad (24a)$$

$$\bar{P}_w = \frac{2S_2^{(1)}}{S_2^{(0)} + 1} + 1 \qquad (24b)$$

$$\bar{P}_z = \frac{3S_2^{(2)} + S_2^{(1)}}{2S_2^{(1)} + S_1^{(0)} + 1} + 1 \qquad (24c)$$

Under the condition $S_3^{(k+1)} \gg S_3^{(k)}$ or $S_2^{(k+1)} \gg S_2^{(k)}$, i.e., in the so-called long-chain limit, these expression degenerate into

$$\bar{P}_n \approx S_2^{(0)} \qquad (25a)$$

$$\bar{P}_w \approx 2S_2^{(1)}/S_2^{(0)} \qquad (25b)$$

$$\bar{P}_z \approx (3/2)S_2^{(2)}/S_2^{(1)} \qquad (25c)$$

As the $S_2^{(k)}$ constitute the various moments of the length distribution of living chains, given by eq 24a–c, so that $\bar{x}_n = S_2^{(1)}/S_2^{(0)}$, $\bar{x}_w = S_2^{(2)}/S_2^{(1)}$, and so on, this means that in the long-chain limit the following interesting relationships exist:

$$\bar{P}_w \approx 2\bar{x}_n \qquad (26a)$$

$$\bar{P}_z \approx (3/2)\bar{x}_w \qquad (26b)$$

Equations 26a and 26b, which in fact are valid for any $F(x,y)$, actually were already contained in the results given for the geometric mean approximation, eq 2, in one of our previous papers.[6] On the other hand, eq 22a had been derived previously from purely kinetic arguments in the course of the numerical treatment of chain transfer in combination with chain length dependent termination.[7] All these relations, which have been referred to in the Introduction, now appear as special cases of a concept of full general validity.

C. Treatment of Termination by Recombination. (i) Termination Exclusively by Recombination. All the relationships so far refer to the chain length distribution and the degrees of polymerization which are obtained with chain transfer and termination by disproportionation as the mechanisms of chain radical stabilization.

If termination is by recombination instead, the two radical chains of lengths x and y involved in the termination process are coupled to give a (dead) polymer molecule of length $P = x + y$. Reorganization of the double sum over x and y appearing in eq 10 into a double sum over x and P under this condition yields

$$\sum_{x=1}^{\infty}\sum_{y=1}^{\infty}F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j = \sum_{P=2}^{\infty}\sum_{x=1}^{P-1}F(x,P-x)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{P-x}\alpha_j$$

Considering further that the number of termination-stabilized polymer chains is reduced to half its value by the coupling reaction due to recombination instead of disproportionation, we now write the full-expression for the chain length distribution of dead polymer as

$$n(P) = D\prod_{i=1}^{P}\alpha_i + (C/2S_1^{(0)})\sum_{x=1}^{P-1}F(x,P-x)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{P-x}\alpha_j \qquad (27)$$

with its moments given by

$$\sum P^k n(P) = D\sum P^k\prod_{i=1}^{P}\alpha_i + (C/2S_1^{(0)})\sum_{P=2}^{\infty}P^k\sum_{x=1}^{P-1}F(x,P-x)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{P-x}\alpha_j \qquad (28)$$

Recalling that $P = x + y$, we can transform the double sum contained in eq 28 back into a double sum of the familiar type

$$\sum_{P=2}^{\infty}P^k\sum_{x=1}^{P-1}F(x,P-x)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{P-x}\alpha_j = \sum_x\sum_y(x+y)^k F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (29)$$

This yields, using the definition of $S_2^{(k)}$ given by eq 18, the following expression for the kth moment of the distribution, eq 27, $S_3^{(k)}$

$$\sum P^k n(P) \equiv S_3^{(k)} = DS_2^{(k)} + (C/2S_1^{(0)})\sum_x\sum_y(x+y)^k F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (30)$$

Introducing a symbol $S_1^{(n,m)}$ for these terms in eq 30 which contain products x^m and y^n, $x^m y^n$,

$$S_1^{(m,n)} \equiv (1/S_1^{(0)})\sum_x\sum_y x^m y^n F(x,y)\prod_{i=1}^{x}\alpha_i\prod_{j=1}^{y}\alpha_j \qquad (31)$$

applying eq 17b and 18, and using symmetry arguments, we write the various moments $S_3^{(k)}$ as

$$S_3^{(0)} = CS_1^{(0)}/2 + DS_2^{(0)} \qquad (32a)$$

$$S_3^{(1)} = CS_1^{(1)} + DS_2^{(1)} \qquad (32b)$$

$$S_3^{(2)} = C(S_1^{(2)} + S_1^{(1,1)}) + DS_2^{(2)} \qquad (32c)$$

$$S_3^{(3)} = C(S_1^{(3)} + 3S_1^{(2,1)}) + DS_2^{(3)} \qquad (32d)$$

(ii) Termination by Recombination *and* Disproportionation. Defining the relative extent of termination by disproportionation by a quantity

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

where $k_{\text{t,dis}}$ is the bimolecular rate constant of mutual termination disproportionation and $k_{\text{t,recomb}}$ is the bimolecular rate constant of mutual termination by recombination, the moments of the chain length distribution of dead polymer may be easily obtained by considering that the contributions to $S_3^{(k)}$ originating from the termination terms $CS_1^{(k)}$ characteristic of disproportionation in eq 20b enter with a weight δ, those characteristic of termination by recombination (eq 32a–d), i.e., $CS_1^{(0)}/2$, $CS_1^{(1)}$, etc., enter with a weight $(1 - \delta)$, and the transfer terms remain unaffected throughout.

This leads to

$$S_3^{(0)} = CS_1^{(0)}(1 + \delta)/2 + DS_2^{(0)} \qquad (34a)$$

$$S_3^{(1)} = CS_1^{(1)} + DS_2^{(1)} \qquad (34b)$$

$$S_3^{(2)} = C(S_1^{(2)} + [1 - \delta]S_1^{(1,1)}) + DS_2^{(2)} \qquad (34c)$$

$$S_3^{(3)} = C(S_1^{(3)} + 3[1 - \delta]S_1^{(2,1)}) + DS_2^{(3)} \qquad (34d)$$

The various averages of the degree of polymerization, $S_3^{(k+1)}/S_3^{(k)}$, for the overall *composite* polymer stabilized by chain transfer and termination by disproportionation *and* recombination accordingly take the general form

$$k = 0\colon\ (\bar{P}_{\text{n}})_{\text{composite}} = \frac{CS_1^{(1)} + DS_2^{(1)}}{CS_1^{(0)}(1 + \delta)/2 + DS_2^{(0)}} \qquad (35)$$

$$k = 1\colon\ (\bar{P}_{\text{w}})_{\text{composite}} = \frac{C(S_1^{(2)} + [1 - \delta]S_1^{(1,1)}) + DS_2^{(2)}}{CS_1^{(1)} + DS_2^{(1)}} \qquad (36)$$

$$k = 2\colon\ (\bar{P}_z)_{\text{composite}} = \frac{C(S_1^{(3)} + 3[1 - \delta]S_1^{(2,1)}) + DS_2^{(3)}}{C(S_1^{(2)} + [1 - \delta]S_1^{(1,1)}) + DS_2^{(2)}} \qquad (37)$$

(iii) Treatment of the Cross Terms $S_1^{(m,n)}$. While comparatively simple expressions are obtained if termination is exclusively by disproportionation (see, for instance, eq 22–25), problems have reached a new dimension upon attempting to incorporate termination by recombination by the appearance of the cross terms $S_1^{(m,n)}$ in the expressions for the weight- and z-average degree of polymerization, eq 36 and 37.

As there is no general way of expressing $S_1^{(m,n)}$ in terms of quantities already known, we have to resort to functions $F(x,y)$ which can be factorized in order to arrive at simple expressions. Thus, if

$$F(x,y) \equiv F(x)F(y) \qquad (38)$$

$S_1^{(m,n)}$, eq 31, can be simplified by performing the two summations involved separately

$$S_1^{(m,n)} = (1/S_1^{(0)})\Big(\sum x^m F(x)\prod_{i=1}^{x}\alpha_i\Big)\Big(\sum y^n F(y)\prod_{j=1}^{y}\alpha_j\Big) = S_1^{(m)}S_1^{(n)}/S_1^{(0)} \qquad (39)$$

This means that $S_1^{(1,1)}$ appearing in eq 32c and 34c might be replaced by $(S_1^{(1)})^2/S_1^{(0)}$, and $S_1^{(2)}S_1^{(1)}/S_1^{(0)}$ would enter into eq 32d and 34d instead of $S_1^{(2,1)}$, respectively, if $F(x,y)$ is actually of the type defined by eq 38. Finally, this would lead to the following modification of the expressions for the weight-average (eq 36) and the z-average (eq 37) degree of polymerization of the overall composite polymer

$$(\bar{P}_{\mathrm{w}})_{\mathrm{composite}} = \frac{C(S_1^{(2)} + [1-\delta](S_1^{(1)})^2/S_1^{(0)}) + DS_2^{(2)}}{CS_1^{(1)} + DS_2^{(2)}} \tag{36a}$$

$$(\bar{P}_z)_{\mathrm{composite}} = \frac{C(S_1^{(3)} + 3[1-\delta]S_1^{(2)}S_1^{(1)}/S_1^{(0)}) + DS_2^{(3)}}{C(S_1^{(2)} + [1-\delta](S_1^{(1)})^2/S_1^{(0)}) + DS_2^{(2)}} \tag{37a}$$

the expression for $(\bar{P}_{\mathrm{n}})_{\mathrm{composite}}$, eq 35, remaining unaffected due to the absence of any cross term.

For the special situation $D = 0$ (no chain transfer) and $\delta = 0$, the general influence of the coupling reaction may be immediately demonstrated on recalling that the $S_1^{(k)}$ are not only the moments of the chain length distribution of disproportionation-terminated polymer but, more generally, of the length distribution of polymer radicals entering termination reaction, irrespective of the termination mode (disproportionation or recombination). Thus, from eq 35, 36a, 37a, and 38 we obtain the expressions

$$(\bar{P}_{\mathrm{n}})_{\delta=0} = 2(\bar{P}_{\mathrm{n}})_{\delta=1} \tag{40a}$$

$$(\bar{P}_{\mathrm{w}})_{\delta=0} = (\bar{P}_{\mathrm{w}})_{\delta=1} + (\bar{P}_{\mathrm{n}})_{\delta=1} \tag{40b}$$

$$(\bar{P}_z)_{\delta=0} = \frac{(\bar{P}_{\mathrm{w}})_{\delta=1}[(\bar{P}_z)_{\delta=1} + 3(\bar{P}_{\mathrm{n}})_{\delta=1}]}{(\bar{P}_{\mathrm{w}})_{\delta=1} + (\bar{P}_{\mathrm{n}})_{\delta=1}} \tag{40c}$$

which nicely show how the "degeneration" present in "classical" polymerization is removed in the case of chain length dependent termination with factorizable $F(x,y)$.

This, however, is not the only consequence if $F(x,y)$ is factorizable. Going back to the original definition of $S_1^{(0)}$, eq 10, or $S_1^{(k)}$, eq 17b, one can easily see that the factorizability of $F(x,y)$ has the favorable effect of making $S_1^{(0)}$ and, accordingly, any $S_1^{(k)}$ immediately representable in terms of a single sum

$$S_1^{(k)} = \sum_x x^k F(x) \prod_{i=1}^{x} \alpha_i \tag{41}$$

Thus, the use of such a function $F(x,y)$ obeying eq 38, for which the geometric mean approximation (eq 2) is the most familiar example, not only results in a substantial simplification of any numerical treatment[2,3,5,7] (as simple expressions for α_i and, accordingly, $S_1^{(k)}$ and $S_2^{(k)}$ might be written down immediately) but also provides the basis for obtaining closed solutions[1-4,6] of the problem of chain length dependent termination if the integrations—which will replace the summations in the long-chain limit—can be performed as is also the case with eq 2[1,6] in the absence of chain transfer even if termination is fully or partly by recombination.

III. Test of the Fundamental Relationships

The fundamental eq 22a–d (or eq 23a–d, respectively) derived in the foregoing section should be valid for any $F(x,y)$. Following the idea that k_{t} is subject to some power law dependence on some mean length $\overline{x,y}$ of the two radicals involved in the termination process[4]

$$k_{\mathrm{t}} = k_{\mathrm{t}}^{\circ}(\overline{x,y})^{-b} \tag{42}$$

we set out to test eq 22 for several distinguished means that can be formulated from the general definition for the mean value of two quantities[8] x and y

$$M \equiv \overline{x,y} = (\tfrac{1}{2}[x^t + y^t])^{1/t} \tag{43}$$

In practice, calculations were carried out for the "means" characterized by the following six values of the parameter t:

$t \to -\infty$: $M_1 = \min\,(x,y)$

$t = -1$: $M_2 = 2xy/(x + y)$ (harmonic mean)

$t = -b$: $M_3 = (\tfrac{1}{2}[x^{-b} + y^{-b}])^{-1/b}$ ("diffusion" mean[9])

$t \to 0$: $M_4 = (xy)^{1/2}$ (geometric mean)

$t = +1$: $M_5 = \tfrac{1}{2}(x + y)$ (arithmetic mean)

$t \to +\infty$: $M_6 = \max\,(x,y)$

With the exception of M_4, which on account of its factorizability leads to a direct solution,[1-4,6] numeric methods as they were originally outlined for the harmonic mean[5,7] had to be applied in all other cases.[10] According to these, the complete set of propagation probabilities $[\alpha_i]$, from which all $S_1^{(k)}$ and $S_2^{(k)}$ may be calculated independently, is evaluated by iteration. The test has been carried out in the following way: Equations 23a–d are rearranged in such a way as to give linear relationships with C^{-1} as the intercept on the ordinate axis and D as the intercept on the abscissa.

$$S_1^{(0)} = C^{-1} - (D/C)S_2^{(0)} \tag{44a}$$

$$S_1^{(1)}/\bar{P}_{\mathrm{n}} = C^{-1} - (D/C)(S_2^{(1)}/\bar{P}_{\mathrm{n}}) \tag{44b}$$

$$S_1^{(2)}/(\bar{P}_{\mathrm{n}}\bar{P}_{\mathrm{w}}) = C^{-1} - (D/C)(S_2^{(2)}/(\bar{P}_{\mathrm{n}}\bar{P}_{\mathrm{w}})) \tag{44c}$$

$$S_1^{(3)}/(\bar{P}_{\mathrm{n}}\bar{P}_{\mathrm{w}}\bar{P}_z) = C^{-1} - (D/C)(S_2^{(3)}/(\bar{P}_{\mathrm{n}}\bar{P}_{\mathrm{w}}\bar{P}_z)) \tag{44d}$$

When the basic data, which are collected in Table I, are plotted in such a way, Figure 1 reveals that actually all points obey these equations. On the other hand, these diagrams may provide further valuable information on the influence exercised by the chain length dependence of k_{t} at a given value of b as well as on the importance that the choice of the mean might have:

(1) As in classical free radical polymerization (where $b = 0$) $S_1^{(k)} = S_2^{(k)}$, the points will lie off this symmetry line if $b \neq 0$ (evidently, the more the larger is $|b|$). Clearly, as k_{t} is assumed to *decrease* with increasing chain lengths ($S_1^{(k)} < S_2^{(k)}$), the points will fall *below* the straight line $S_1^{(k)} = S_2^{(k)}$.

(2) The deviations from this straight line are lowest for M_1 and largest for M_6. It is seen, however, that the points corresponding to different means lie rather close to each other. This refers in particular to the points corresponding to M_2–M_5, and within this group, most impressively to M_3 and M_4, which can be resolved only with difficulty on the scale of Figure 1. Actually, in the course of some earlier work,[11] Ito had offered some arguments for the close similarity of M_3 and M_4 when he replaced M_3 by the more tractable geometric mean M_4. The obvious reason for this peculiar behavior, however, simply lies in the close neighborhood of the t values characterizing the geometric mean (M_4) and the "diffusion" mean (M_3) if b does not differ too much from 0 (moderate dependence of k_{t} on $\overline{x,y}$). This makes it reasonable to use M_4 in place of M_3 in this case with strongly limited losses in accuracy.

IV. Applications

A. Preliminaries. The complete solution of the kinetic scheme involves the knowledge of all $S_1^{(k)}$, $S_2^{(k)}$, and $S_3^{(k)}$, and, in addition, if $F(x,y)$ cannot be factorized, also of all $S_1^{(m,n)}$, when termination is partly or fully by recombination. As was outlined already in previous papers[1,7] all relevant kinetic quantities can be easily expressed in terms of the above-mentioned moments. This refers particularly to the so-called "apparent" termination rate constant $\overline{k_{\mathrm{t}}}$,

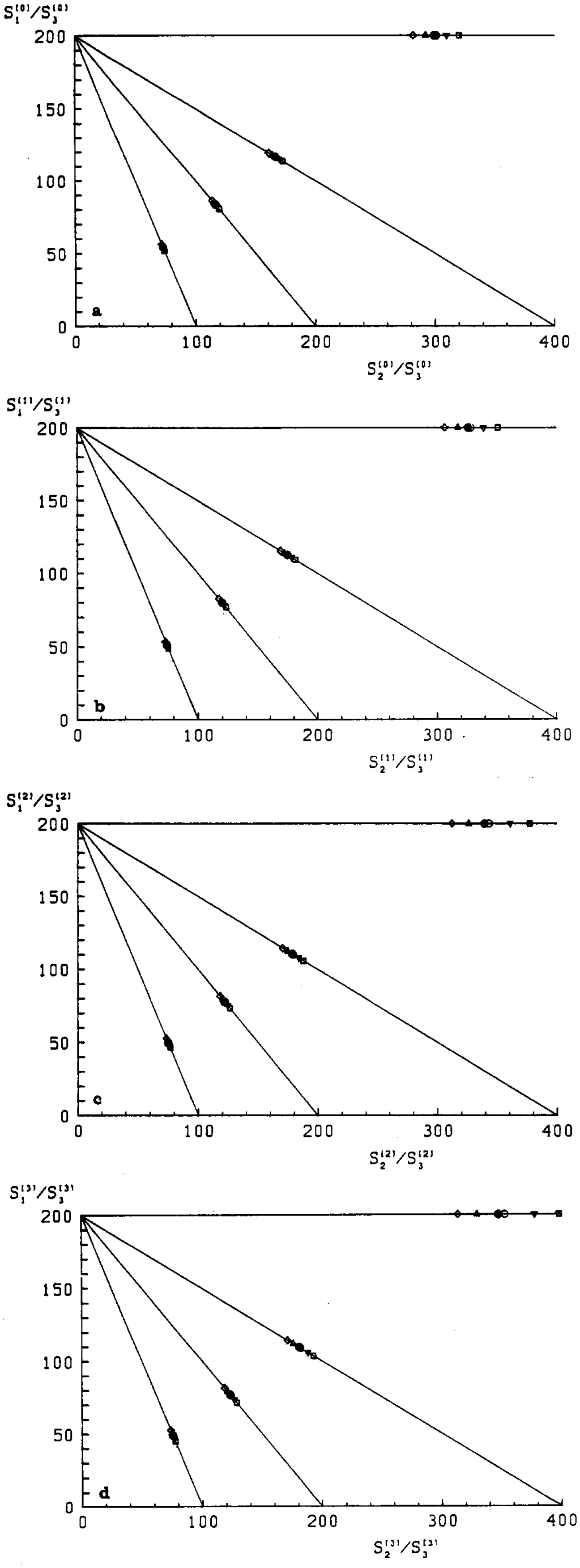

Figure 1. Plots of $S_1^{(k)}/S_3^{(k)}$ vs. $S_2^{(k)}/S_3^{(k)}$ (with $S_3^{(k)} = CS_1^{(k)} + DS_2^{(k)}$) for the means M_1 (◇), M_2 (△), M_3 (●), M_4 (○), M_5 (▽), and M_6 (□) with $b = 0.16$, $C = 0.005$, and $D = 0$, 0.0025, 0.0005, and 0.0010. (a) $k = 0$ ($S_3^{(0)} = 1$); (b) $k = 1$ ($S_3^{(1)} = \bar{P}_n$); (c) $k = 2$ ($S_3^{(2)} = \bar{P}_n\bar{P}_w$); (d) $k = 3$ ($S_3^{(3)} = \bar{P}_n\bar{P}_w\bar{P}_z$). Points referring to classical polymerization ($b = 0$) would appear on the symmetry line $S_1^{(k)} = S_2^{(k)}$ (not shown in the figures).

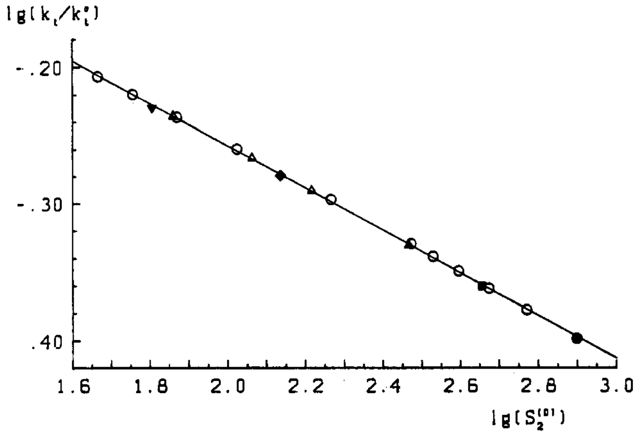

Figure 2. Double-logarithmic plots of $\bar{k}_t/k_t°$ vs. $S_2^{(0)}$ for the harmonic mean approximation with $b = 0.16$. Full symbols: $D = 0$, $C = 0.002$ (●), $C = 0.00333$ (■), $C = 0.005$ (▲), $C = 0.01$ (◆), $C = 0.02$ (▼); open symbols: $0.0004 \leq D \leq 0.02$, $C = 0.002$ (○); $0.0025 \leq D \leq 0.01$, $C = 0.005$ (△).

defined by $\overline{k_t} = v_0/(\sum[R_i])^2$, which for $\delta = 1$ is related to $S_1^{(0)}$ and $S_2^{(0)}$ by the simple relationship

$$\overline{k_t}/k_t° = (S_1^{(0)}/S_2^{(0)})^2 \tag{45}$$

Actually, $\overline{k_t}/k_t°$ is found to exhibit the same general form as a function of the average degree of polymerization as does the function $\overline{F(x,y)}$ in polymerization systems without chain transfer at least as long as $F(x,y)$ varies monotonously with x and y.[12] Concretely, this means that eq 42 transposes itself into

$$\overline{k_t}/k_t° = \text{const} \times \bar{P}^{-b} \tag{46}$$

with the numerical value of the constant (which is of the order of unity) depending on the type of mean $\overline{(x,y)}$ and on the type of average $\bar{P}$ inserted.

As a further important point, in systems with termination exclusively by disproportionation, the validity of eq 46 is nearly unaffected by the occurrence of chain transfer[7] so that eq 46 can be considered to exhibit a fairly universal character as long as each dead polymer molecule consists of only one independently grown chain. In fact, there is a few percent variation of the constant in eq 46 for moderate b values when the system shifts from the limit $D = 0$ (no transfer) to the limit $D \gg C$ (predominant transfer). In order to show that this is not a peculiarity of the geometric mean assumption, as a further example of this astonishing behavior, data corresponding to the harmonic mean assumption are plotted according to eq 46 on a double-logarithmic scale in Figure 2. This demonstrates that all points, those for $D = 0$ and those for $D \gg C$, can be accommodated by a single straight line of slope $-b$ within the resolution of the diagram. As in the long-chain limit $\bar{P}_n$ may be replaced by $S_2^{(0)}$ (eq 24a), eq 45 can be rewritten in the form

$$\overline{k_t}/k_t° = (S_2^{(0)})^{-b}(S_1^{(0)})^2/(S_2^{(0)})^{2-b} \tag{45a}$$

which implies that the ratio $(S_1^{(0)})^2/(S_2^{(0)})^{2-b}$—on comparison with eq 46—and, accordingly, also the ratio $S_1^{(0)}/(S_2^{(0)})^{1-b/2}$, are fairly constant and practically independent of D. It is this outstanding property which, on combination with the fundamental eq 22 and 23, allows us to give a surprisingly good solution of the kinetic scheme.

B. Geometric Mean Approximation in the Long-Chain Limit. Due to their factorizability closed solutions are available for $S_1^{(k)}$ and $S_2^{(k)}$ for $D = 0$.[1-3,6] The general

Table I
Compilation of $S_1^{(k)}$ and $S_2^{(k)}$ for Various Values of the Parameter t (C = 0.005, b = 0.16)

t	$S_2^{(0)}/10^2$	$S_2^{(1)}/10^5$	$S_2^{(2)}/10^7$	$S_2^{(3)}/10^{11}$	$S_1^{(0)}/10^2$	$S_1^{(1)}/10^4$	$S_1^{(2)}/10^7$	$S_1^{(3)}/10^{10}$	$S_1^{(1,1)}/10^7$	$S_1^{(2,1)}/10^{10}$
$D = 0$										
$-\infty$	2.8240	0.8698	5.4473	0.5146	2.0000	5.6681	3.4847	3.2736	1.5277	0.9178
-1	2.9265	0.9344	6.1119	0.6070	2.0000	5.8729	3.7435	3.6728	1.6659	1.0447
$-b$	2.9970	0.9820	6.6810	0.6989	2.0000	6.0141	3.9341	4.0145	1.7939	1.1689
0	3.0156	0.9951	6.8475	0.7276	2.0000	6.0512	3.9864	4.1145	1.8308	1.2061
$+1$	3.1006	1.0558	7.6353	0.8679	2.0000	6.2212	4.2292	4.5868	1.9978	1.3802
$+\infty$	3.2067	1.1313	8.5527	1.0250	2.0000	6.4334	4.5312	5.1367	2.1680	1.5634
t	$S_2^{(0)}/10^2$	$S_2^{(1)}/10^4$	$S_2^{(2)}/10^7$	$S_2^{(3)}/10^9$	$S_1^{(0)}/10^2$	$S_1^{(1)}/10^4$	$S_1^{(2)}/10^6$	$S_1^{(3)}/10^9$	$S_1^{(1,1)}/10^6$	$S_1^{(2,1)}/10^9$
$D = C/2$										
$-\infty$	1.6121	2.7423	0.9399	4.8481	1.1939	1.8731	6.3019	3.2320	2.7993	0.9207
-1	1.6451	2.8543	1.0018	5.3105	1.1774	1.8831	6.4413	3.3727	2.9137	0.9811
$-b$	1.6668	2.9313	1.0501	5.7181	1.1666	1.8879	6.5084	3.4591	3.0321	1.0414
0	1.6723	2.9515	1.0634	5.8351	1.1638	1.8888	6.5230	3.4803	3.0654	1.0586
$+1$	1.6975	3.0438	1.1234	6.3664	1.1512	1.8932	6.5920	3.5755	3.2078	1.1338
$+\infty$	1.7290	3.1568	1.1908	6.9205	1.1355	1.8996	6.7078	3.7031	3.3202	1.1986
t	$S_2^{(0)}/10^2$	$S_2^{(1)}/10^4$	$S_2^{(2)}/10^6$	$S_2^{(3)}/10^9$	$S_1^{(0)}/10^1$	$S_1^{(1)}/10^3$	$S_1^{(2)}/10^6$	$S_1^{(3)}/10^8$	$S_1^{(1,1)}/10^6$	$S_1^{(2,1)}/10^8$
$D = C$										
$-\infty$	1.1357	1.3456	3.1984	1.1430	8.6430	9.4585	2.2068	7.8412	0.9868	2.2512
-1	1.1522	1.3841	3.3450	1.2185	8.4785	9.4024	2.2145	7.9680	1.0096	2.3411
$-b$	1.1626	1.4097	3.4551	1.2820	8.3735	9.3556	2.2073	7.9952	1.0377	2.4394
0	1.1653	1.4163	3.4846	1.2997	8.3472	9.3422	2.2043	7.9963	1.0456	2.4670
$+1$	1.1774	1.4465	3.6171	1.3784	8.2259	9.2833	2.1925	8.0052	1.0785	2.5848
$+\infty$	1.1926	1.4835	3.7647	1.4592	8.0736	9.2180	2.1932	8.0852	1.0984	2.6704
t	$S_2^{(0)}/10^1$	$S_2^{(1)}/10^3$	$S_2^{(2)}/10^5$	$S_2^{(3)}/10^8$	$S_1^{(0)}/10^1$	$S_1^{(1)}/10^3$	$S_1^{(2)}/10^5$	$S_1^{(3)}/10^8$	$S_1^{(1,1)}/10^5$	$S_1^{(2,1)}/10^7$
$D = 2C$										
$-\infty$	7.1736	5.3297	7.9032	1.7605	5.6527	3.8878	5.6581	1.2531	2.5522	3.6324
-1	7.2400	5.4264	8.1317	1.8335	5.5200	3.8273	5.5890	1.2446	2.5720	3.6989
$-b$	7.2809	5.4886	8.2968	1.8923	5.4383	3.7846	5.5083	1.2266	2.6155	3.7934
0	7.2909	5.5043	8.3399	1.9081	5.4181	3.7733	5.4851	1.2209	2.6278	3.8199
$+1$	7.3378	5.5762	8.5334	1.9781	5.3244	3.7232	5.3868	1.1974	2.6777	3.9297
$+\infty$	7.3979	5.6655	8.7495	2.0495	5.2042	3.6648	5.3128	1.1848	2.6904	3.9836

result for the (equally constant) ratio under these conditions, $(A_k)_{D=0} \equiv (S_2^{(0)})^{b/2}S_2^{(k)}$, is

$$(S_2^{(0)})^{b/2}S_1^{(k)}/S_2^{(k)} \equiv (A_k)_{D=0} = \left(\Gamma\frac{4-b}{2-b}\right)^{b/2}\Gamma\frac{2k+2-b}{2-b}\Bigg/\Gamma\frac{2k+2}{2-b} \quad (47)$$

As eq 47 holds fairly well also for $D > 0$, it may be combined with eq 22a to give an equation that contains $S_2^{(0)}$ as the only variable

$$S_2^{(0)}[CA_0(S_2^{(0)})^{-b/2} + D] = 1 \quad (48)$$

which might be easily solved for $S_2^{(0)}$ by iteration. The long-chain-limit version of eq 22b ($S_2^{(0)} \gg 1$) now may be written in the form

$$C(S_1^{(1)}/S_2^{(0)}) + D(S_2^{(1)}/S_2^{(0)}) = 1 \quad (49)$$

Recalling that $S_1^{(1)}/S_1^{(0)}$ is the number-average degree of polymerization $\bar{T}_n$ of disproportionation-terminated polymer and $S_2^{(1)}/S_2^{(0)}$ is that of living or transfer-stabilized polymer, $\bar{x}_n$, we find that combination with eq 47 (for k = 0) leads to

$$C\bar{T}_nA_0(S_2^{(0)})^{-b/2} + D\bar{x}_n = 1 \quad (49a)$$

Finally, considering that $\bar{x}_n/\bar{T}_n = A_1/A_0$ (eq 47), we may now solve eq 49a for $\bar{x}_n$

$$\bar{x}_n = (CA_1(S_2^{(0)})^{-b/2} + D)^{-1} \quad (49b)$$

Along similar lines eq 22c and 22d may also be transformed to give

$$C\bar{T}_wA_1(S_2^{(0)})^{-b/2} + D\bar{x}_w = \bar{x}_w(CA_2(S_2^{(0)})^{-b/2} + D) = 2 \quad (50)$$

and

$$C\bar{T}_zA_2(S_2^{(0)})^{-b/2} + D\bar{x}_z = \bar{x}_z(CA_3(S_2^{(0)})^{-b/2} + D) = 3 \quad (51)$$

respectively, to yield $\bar{x}_w$ and $\bar{x}_z$. $\bar{T}_n$, $\bar{T}_w$, and $\bar{T}_z$ now may be evaluated from $\bar{x}_n$, $\bar{x}_w$, and $\bar{x}_z$ by using eq 49, 50, and 51.

Values for the most important kinetic quantities calculated by this method (A) for b = 0.05, 0.16, and 0.25 for several values of D at C = 0.0005 may be compared with data obtained from series-expansion solutions[1,7] (code E) in Table II.

The agreement in fact is rather good for small values of b but diminishes on going to larger b (b = 0.25). This points to the fact that the only assumption that is inherent, namely, that A_k is fully independent of D, becomes less appropriate with increasing deviation from "classical" polymerization.

Numeric calculations along the lines described in ref 7 carried out for very low C values ($C \approx 10^{-5}$, which in practice correspond to very low rates of initiation and, accordingly, to high kinetic chain lengths) and D values up to $D = 10C$ (corresponding to a moderate extent of chain transfer to that still "high" polymer is formed) have revealed that the A_k values vary linearly with $S_2^{(0)}$ (or $\bar{P}_n$). This outstanding behavior is represented in Figure 3. Translating these results, which are obtained for long chains (but not in the long-chain limit), to the long-chain limit itself, this means that there the apparent A_k values should vary linearly with $S_2^{(0)}$ from those characteristic of systems devoid of chain-transfer agents (D = 0), which are described by eq 47, to those representative for the limit $D \gg C$, which in the long-chain limit are given by

$$(S_2^{(0)})^{b/2}S_1^{(k)}/S_2^{(k)} \equiv (A_k)_{D\gg C} = \Gamma(1 + k - (b/2))/k! \quad (52)$$

Thus

$$(A_k)_{\text{app}} = (A_k)_{D\gg C} + [(S_2^{(0)})_{D>0}/(S_2^{(0)})_{D=0}][(A_k)_{D=0} - (A_k)_{D\gg C}] \quad (53)$$

Table II

Influence of Chain Transfer on Kinetic Data and Degrees of Polymerization for Various Extents of Chain Length Dependence of k_t ($C = 0.0005$) in the Long-Chain Limit of the Geometric Mean Approximation: Comparison of Data Obtained by Termwise Integration of the Series Expansion of the Chain Length Distribution[7] (Code E) with Those Obtained from Eq 49–51, $A_k = (A_k)_{D\to 0}$ (Code A), and $A_k = (A_k)_{\mathrm{app}}$ (Code B)

				living chains			disproportionation + transfer			recombination + transfer		
code	$D/10^{-4}$	ν	$\bar{k}_t/k_t^\circ$	$\bar{x}_n$	$\bar{x}_w/\bar{x}_n$	$\bar{x}_z/\bar{x}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	$\bar{P}_z/\bar{P}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	$\bar{P}_z/\bar{P}_w$
$b = 0.05$												
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
A,B		2394.5	0.6977	2456.8	2.0258	1.5129	2394.5	2.0521	1.5193	4789.0	1.5260	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
A		2387.6	0.7017	2182.4	2.0229	1.5114	2132.9	2.0464	1.5172	3854.8	1.6239	1.3700
B		2387.4	0.7018	2182.2	2.0229	1.5114	2132.8	2.0463	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
A		2366.1	0.7145	1510.8	2.0160	1.5079	1486.7	2.0324	1.5120	2167.7	1.8166	1.4232
B		2365.7	0.7147	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
A		2347.3	0.7260	1092.6	2.0116	1.5058	1079.9	2.0236	1.5087	1402.5	1.9026	1.4536
B		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	1.4776
A		2321.9	0.7420	704.35	2.0076	1.5037	698.97	2.0154	1.5057	822.81	1.9587	1.4776
B		2321.1	0.7425	704.22	2.0075	1.5037	698.89	2.0152	1.5056	822.76	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
A		2245.6	0.7932	184.03	2.0020	1.5010	183.64	2.0042	1.5015	191.47	1.9970	1.4980
B		2244.6	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
A,B		3679.0	0.2955	4017.1	2.0893	1.5443	3679.0	2.1838	1.5670	7358.01	1.5919	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
A		3626.1	0.3042	3305.0	2.0740	1.5365	3069.6	2.1534	1.5555	5322.3	1.7167	1.4099
B		3623.3	0.3047	3300.8	2.0732	1.5361	3067.6	2.1521	1.5549	5319.3	1.7160	1.4095
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
A		3484.0	0.3295	1949.8	2.0448	1.5219	1862.1	2.0942	1.5336	2541.2	1.8947	1.4580
B		3476.1	0.3310	1945.3	2.0434	1.5212	1859.9	2.0919	1.5326	2539.1	1.8935	1.4572
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
A		3375.9	0.3510	1296.5	2.0305	1.5148	1255.9	2.0646	1.5229	1543.0	1.9513	1.4780
B		3365.9	0.3531	1293.8	2.0293	1.5142	1254.6	2.0626	1.5220	1541.9	1.9504	1.4774
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
A		3244.4	0.3800	779.86	2.0190	1.5092	764.40	2.0405	1.5142	866.47	1.9816	1.4908
B		3233.0	0.3827	778.64	2.0181	1.5088	763.76	2.0389	1.5136	866.06	1.9810	1.4904
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
A		2898.9	0.4760	188.11	2.0051	1.5025	187.09	2.0109	1.5038	193.33	1.9990	1.4994
B		2886.9	0.4800	188.02	2.0048	1.5023	187.04	2.0104	1.5036	193.30	1.9989	1.4994
$b = 0.25$												
E	0.0	5436.7	0.1353	6289.0	2.1489	1.5733	5436.7	2.3135	1.6116	10873.4	1.6568	1.4178
A,B		5436.6	0.1353	6288.9	2.1491	1.5732	5436.6	2.3135	1.6118	10873.2	1.6568	1.4179
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
A		5258.3	0.1447	4664.1	2.1123	1.5545	4163.6	2.2404	1.5843	6892.4	1.8020	1.4450
B		5243.4	0.1455	4643.7	2.1097	1.5532	4154.3	2.2356	1.5823	6879.6	1.7993	1.4434
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
A		4853.3	0.1698	2335.8	2.0594	1.5283	2192.8	2.1304	1.5446	2832.7	1.9457	1.4810
B		4820.2	0.1721	2322.0	2.0563	1.5268	2186.0	2.1245	1.5422	2827.0	1.9428	1.4791
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
A		4585.5	0.1902	1452.4	2.0387	1.5183	1392.6	2.0858	1.5290	1641.9	1.9785	1.4918
B		4547.4	0.1934	1445.4	2.0363	1.5172	1389.1	2.0812	1.5272	1639.5	1.9766	1.4905
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
A		4285.7	0.2178	832.15	2.0236	1.5111	810.81	2.0526	1.5177	895.52	1.9933	1.4974
B		4245.7	0.2219	829.38	2.0219	1.5103	809.37	2.0494	1.5164	894.64	1.9923	1.4967
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
A		3573.4	0.3132	190.77	2.0064	1.5030	189.40	2.0145	1.5048	194.56	2.0002	1.5002
B		3536.2	0.3199	190.57	2.0059	1.5028	189.29	2.0135	1.5044	194.50	2.0000	1.5001

where $(S_2^{(0)})_{D=0}$ refers to the value of $(S_2^{(0)})$ observed in the absence of chain transfer under the same rate of initiation (same C).

Inserting these $(A_k)_{\mathrm{app}}$ for A_k in eqs 48–52, we obtain long-chain-limit kinetic quantities in this way (method B) which show perfect agreement with the "exact" values (E) obtained from series expansions[7] even when the extent of the chain length dependence, expressed by the parameter b, increases. Thus, by application of the fundamental relationships derived in the previous section together with the favorable consequences that the geometric mean assumption has for the treatment of termination by recombination, an "exact" solution is obtained for this case in the long-chain limit which is free from approximations. The only empirical feature inherent in this treatment is the assumption of the validity of eq 52, which, however, may be considered to be perfectly proved by the plots given in Figure 3, especially when the extended scale of the ordinate is taken into account.

C. Other Types of Means. The situation in this case is by far less favorable than for the geometric mean, as for the means defined in the beginning of this section, other than the geometric mean in the long-chain approximation (at least at present), no closed expressions are available

Table III

Compilation of Kinetic Data for Various Means ($-\infty \leqslant t \leqslant +\infty$) with C = 0.005 and b = 0.16: Exact Numeric Solution (Code N), Using Fundamental Equations in Their Long Chain Approximation (Code A1), Using Fundamental Equations in Their Exact Form (Code A2)

				living chains			disproportionation + transfer			recombination + transfer		
t	code	ν	$\overline{k_t}/k_t^\circ$	$\bar{x}_n$	$\bar{x}_w/\bar{x}_n$	$\bar{x}_z/\bar{x}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	$\bar{P}_z/\bar{P}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	$\bar{P}_z/\bar{P}_w$
$D = 0$												
$-\infty$	N	282.40	0.5016	307.98	2.0336	1.5084	283.40	2.1693	1.5280	566.81	1.5602	1.3597
	A1	281.47	0.5049	306.68	2.0372	1.5085	281.47	2.1791	1.5279	562.95	(1.5896)	(1.3647)
	A2	281.47	0.5049	307.77	2.0333	1.5084	282.47	2.1749	1.5279	564.95	(1.5875)	(1.3643)
-1	N	292.65	0.4671	319.30	2.0485	1.5184	293.65	2.1707	1.5392	587.29	1.5684	1.3662
	A1	291.78	0.4699	318.00	2.0521	1.5184	291.78	2.1797	1.5391	583.55	(1.5899)	(1.3700)
	A2	291.78	0.4699	319.09	2.0483	1.5183	292.78	2.1757	1.5390	585.55	(1.5878)	(1.3696)
$-b$	N	299.70	0.4453	327.66	2.0763	1.5376	300.70	2.1754	1.5599	601.41	1.5837	1.3786
	A1	299.12	0.4471	326.46	2.0799	1.5376	299.12	2.1828	1.5600	598.24	(1.5914)	(1.3801)
	A2	299.12	0.4471	327.55	2.0762	1.5375	300.12	2.1789	1.5599	600.24	(1.5894)	(1.3797)
0	N	301.56	0.4399	329.98	2.0854	1.5441	302.56	2.1773	1.5668	605.12	1.5887	1.3828
	A1	301.10	0.4412	328.83	2.0892	1.5442	301.10	2.1841	1.5669	602.21	1.5921	1.3835
	A2	301.10	0.4412	329.92	2.0855	1.5441	302.10	2.1802	1.5668	604.21	1.5901	1.3831
$+1$	N	310.06	0.4161	340.51	2.1239	1.5718	311.06	2.1855	1.5954	622.12	1.6089	1.4002
	A1	309.90	0.4165	339.45	2.1283	1.5732	309.90	2.1907	1.5962	619.79	(1.5954)	(1.3980)
	A2	309.90	0.4165	340.54	2.1246	1.5731	310.90	2.1869	1.5961	621.79	(1.5934)	(1.3975)
$+\infty$	N	320.67	0.3890	352.78	2.1431	1.5852	321.67	2.1896	1.6095	643.34	1.6186	1.4087
	A1	320.53	0.3893	351.72	2.1478	1.5877	320.53	2.1946	1.6109	641.05	(1.5973)	(1.4054)
	A2	320.53	0.3893	352.82	2.1442	1.5875	321.53	2.1909	1.6107	643.05	(1.5955)	(1.4049)
$D = C/2$												
$-\infty$	N	270.05	0.5485	170.10	2.0150	1.5049	162.21	2.0905	1.5161	231.23	1.8397	1.4339
	A1	269.16	0.5521	169.21	2.0213	1.5049	160.89	2.1033	1.5160	229.48	(1.8652)	(1.4404)
	A2	269.16	0.5521	170.26	2.0147	1.5048	161.89	2.0965	1.5159	230.91	(1.8604)	(1.4400)
-1	N	279.45	0.5122	173.50	2.0229	1.5103	165.51	2.0899	1.5219	234.56	1.8500	1.4393
	A1	278.67	0.5151	172.63	2.0293	1.5103	164.24	2.1022	1.5220	232.87	(1.8693)	(1.4442)
	A2	278.67	0.5151	173.68	2.0229	1.5102	165.24	2.0955	1.5219	234.29	(1.8646)	(1.4438)
$-b$	N	285.75	0.4899	175.87	2.0369	1.5201	167.68	2.0911	1.5324	236.72	1.8632	1.4474
	A1	285.43	0.4910	175.13	2.0442	1.5205	166.57	2.1028	1.5331	235.20	(1.8727)	(1.4496)
	A2	285.43	0.4910	176.18	2.0378	1.5204	167.57	2.0962	1.5330	236.61	(1.8681)	(1.4492)
0	N	287.37	0.4844	176.50	2.0412	1.5231	168.23	2.0917	1.5356	237.27	1.8671	1.4499
	A1	287.26	0.4847	175.82	2.0490	1.5240	167.19	2.1032	1.5368	235.82	1.8738	1.4514
	A2	287.26	0.4847	176.87	2.0426	1.5239	168.19	2.0966	1.5367	237.23	1.8691	1.4509
$+1$	N	294.91	0.4599	179.30	2.0585	1.5354	170.75	2.0937	1.5484	239.76	1.8829	1.4598
	A1	295.35	0.4586	178.86	2.0690	1.5385	169.90	2.1054	1.5517	238.50	(1.8784)	(1.4586)
	A2	295.35	0.4586	179.91	2.0626	1.5383	170.90	2.0990	1.5516	239.90	(1.8738)	(1.4581)
$+\infty$	N	304.54	0.4313	182.58	2.0661	1.5407	173.90	2.0935	1.5540	242.83	1.8923	1.4650
	A1	305.11	0.4297	182.25	2.0779	1.5449	173.08	2.1060	1.5584	241.62	(1.8828)	(1.4627)
	A2	305.11	0.4297	183.31	2.0716	1.5448	174.08	2.0996	1.5582	243.01	(1.8783)	(1.4622)
$D = C$												
$-\infty$	N	262.80	0.5792	118.48	2.0063	1.5035	114.57	2.0589	1.5115	146.15	1.9087	1.4595
	A1	261.72	0.5840	117.55	2.0152	1.5035	113.37	2.0738	1.5114	144.71	(1.9320)	(1.4657)
	A2	261.72	0.5840	118.59	2.0060	1.5034	114.37	2.0644	1.5113	145.99	(1.9247)	(1.4654)
-1	N	271.78	0.5415	120.13	2.0118	1.5073	116.22	2.0582	1.5155	147.47	1.9164	1.4638
	A1	270.84	0.5453	119.22	2.0207	1.5073	115.05	2.0726	1.5156	146.07	(1.9349)	(1.4684)
	A2	270.84	0.5453	120.26	2.0117	1.5072	116.05	2.0633	1.5155	147.34	(1.9276)	(1.4680)
$-b$	N	277.70	0.5187	121.25	2.0213	1.5139	117.27	2.0589	1.5226	148.31	1.9262	1.4698
	A1	277.33	0.5201	120.43	2.0311	1.5144	116.20	2.0727	1.5233	147.00	(1.9372)	(1.4718)
	A2	277.33	0.5201	121.46	2.0221	1.5143	117.20	2.0636	1.5232	148.26	(1.9299)	(1.4714)
0	N	279.21	0.5131	121.55	2.0242	1.5160	117.53	2.0593	1.5247	148.52	1.9290	1.4716
	A1	279.08	0.5136	120.76	2.0344	1.5167	116.51	2.0730	1.5258	147.24	1.9378	1.4729
	A2	279.08	0.5136	121.79	2.0255	1.5166	117.51	2.0638	1.5257	148.50	1.9306	1.4725
$+1$	N	286.27	0.4881	122.85	2.0355	1.5240	118.74	2.0603	1.5331	149.48	1.9404	1.4787
	A1	286.83	0.4862	122.21	2.0480	1.5266	117.84	2.0742	1.5360	148.30	(1.9408)	(1.4774)
	A2	286.83	0.4862	123.24	2.0391	1.5264	118.84	2.0651	1.5359	149.56	(1.9336)	(1.4769)
$+\infty$	N	295.44	0.4583	124.39	2.0402	1.5273	120.26	2.0597	1.5366	150.68	1.9470	1.4825
	A1	296.18	0.4560	123.81	2.0539	1.5308	119.38	2.0741	1.5404	149.52	(1.9436)	(1.4800)
	A2	296.18	0.4560	124.85	2.0450	1.5306	120.38	2.0652	1.5402	150.77	(1.9365)	(1.4795)
$D = 2C$												
$-\infty$	N	253.81	0.6209	74.296	1.9959	1.5022	72.737	2.0286	1.5074	84.707	1.9490	1.4789
	A1	252.28	0.6285	73.324	2.0098	1.5022	71.613	2.0478	1.5073	83.459	(1.9722)	(1.4841)
	A2	252.28	0.6285	74.348	1.9956	1.5022	72.613	2.0333	1.5073	84.624	(1.9599)	(1.4837)
-1	N	262.32	0.5813	74.950	1.9994	1.5047	73.400	2.0280	1.5100	85.151	1.9539	1.4818
	A1	260.96	0.5874	73.987	2.0133	1.5046	72.296	2.0468	1.5100	83.921	(1.9737)	(1.4855)
	A2	260.96	0.5874	75.010	1.9993	1.5046	73.296	2.0325	1.5099	85.082	(1.9614)	(1.4852)
$-b$	N	267.76	0.5579	75.384	2.0053	1.5088	73.809	2.0286	1.5143	85.422	1.9602	1.4858
	A1	267.13	0.5605	74.461	2.0198	1.5092	72.762	2.0467	1.5149	84.234	(1.9748)	(1.4873)
	A2	267.13	0.5605	75.484	2.0058	1.5090	73.762	2.0325	1.5147	85.391	(1.9625)	(1.4870)
0	N	269.13	0.5522	75.495	2.0070	1.5100	73.909	2.0288	1.5156	85.489	1.9619	1.4869
	A1	268.80	0.5536	74.591	2.0219	1.5106	72.885	2.0468	1.5165	84.316	1.9751	1.4879
	A2	268.80	0.5536	75.614	2.0079	1.5105	73.885	2.0326	1.5163	85.473	1.9629	1.4875

Table III (Continued)

t	code	ν	$\overline{k_t}/k_t^\circ$	living chains			disproportionation + transfer			recombination + transfer		
				$\bar{x}_n$	$\bar{x}_w/\bar{x}_n$	$\bar{x}_z/\bar{x}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	$\bar{P}_z/\bar{P}_w$	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	$\bar{P}_z/\bar{P}_w$
+1	N	275.63	0.5265	75.993	2.0138	1.5148	74.378	2.0294	1.5206	85.799	1.9691	1.4915
	A1	276.17	0.5244	75.156	2.0304	1.5167	73.417	2.0474	1.5228	84.671	(1.9766)	(1.4902)
	A2	276.17	0.5244	76.180	2.0165	1.5166	74.417	2.0333	1.5226	85.824	(1.9644)	(1.4898)
+∞	N	284.30	0.4949	76.583	2.0166	1.5167	74.979	2.0289	1.5226	86.193	1.9731	1.4939
	A1	285.07	0.4922	75.776	2.0339	1.5192	74.032	2.0471	1.5254	85.078	(1.9780)	(1.4916)
	A2	285.07	0.4922	76.800	2.0200	1.5191	75.032	2.0332	1.5252	86.228	(1.9658)	(1.4911)

Table IV
Preexponential Factors A_k of the Power Laws $S_1^{(k)}/S_2^{(k)} = A_k(S_2^{(0)})^{-b/2}$ for Various Values of the Parameter t (b = 0.16) Obtained by Extrapolating A_k Values for D = 0 to Infinite Chain Length

t	A_0	A_1	A_2	A_3
$-\infty$	1.1157	1.0240	1.0053	0.9996
-1	1.0794	0.9904	0.9652	0.9536
$-b$	1.0550	0.9666	0.9295	0.9068
0	1.0485	0.9602	0.9192	0.8929
+1	1.0212	0.9323	0.8761	0.8353
$+\infty$	0.9900	0.9022	0.8401	0.7937

for A_k either in the limit $D = 0$ or in the limit $D \gg C$. All that can be done in these cases is to evaluate $(A_k)_{D=0}$ by iteration by the procedures described earlier.[5,7] Due to the huge calculational expenditure that is connected with this method, the procedure can be carried out only for comparatively short chains so that A_k values either refer to finite chain length or have to be extrapolated to infinite chain length.

Once the A_k values have been evaluated in one of these ways, the influence that chain-transfer agents exercise on the relevant kinetic quantities may be estimated along the lines outlined in the preceding paragraph (method A), making use of the fundamental equations, eq 22 and 23, and again assuming that $(A_k)_{D\gg C}$ will not differ sensibly from $(A_k)_{D=0}$.

Table III summarizes the results of this procedure obtained by using the fundamental equations in the long-chain limit (A1) and taking the exact short-chain forms (A2). In both cases the A_k values for $D = 0$ extrapolated to infinite chain length have been inserted (Table IV). Comparison with the (exact) data evaluated numerically (N) from the chain length distributions obtained by iteration clearly shows that the use of the long-chain approximation is not fully justified in view of the rather small chain lengths dealt with in this case. The agreement is markedly improved in case A2 when the treatment is based on the exact fundamental equations. However, even here the agreement with the exact values is somewhat less convincing than it is for the long-chain-limit data of the geometric mean approximation described in the preceding paragraph. This, among other reasons, is to be attributed to the neglect of the difference between $(A_k)_{D=0}$ and $(A_k)_{D\gg C}$, which, of course, is rather important in the range of chain lengths investigated here. As the geometric mean (with the appropriate short-chain data) has been included in this treatment, it might be easily verified that this lower level of agreement has little to do with the type of mean adopted but seems to be a general feature of the procedure when applied under these somewhat unfavorable conditions.

One further point of high interest, however, is the question of whether the general formalism of evaluating the $\bar{P}_w$ and $\bar{P}_z$ data of recombination-terminated polymer, which has been developed for the factorizable geometric mean assumption in section II·C, might be applied as an approximation for the other means. Unfortunately, however, as may be deduced from Table III, this approximation does not work extremely well. Again the disturbing influence exercised by the somewhat unfavorable conditions that govern the procedure outlined in this paragraph might be separated from the (partial) failure of this approximation by comparing the results for $\bar{P}_w/\bar{P}_n$ and $\bar{P}_z/\bar{P}_w$ obtained for the geometric mean assumption to those obtained for the other means ($\bar{P}_n$ is reproduced correctly in any case, as it must be double the $\bar{P}_n$ of disproportionation-terminated polymer). While the agreement is quite good for the small t value characterizing the "diffusion" mean M_3, which is very close to the geometric mean M_4 with $t = 0$, for which the formalism is fully correct, the situation is much less satisfactory for the arithmetic and the harmonic mean and, especially, for the extreme t values that characterize M_1 and M_6.

V. Discussion of Numeric Results and Their Relevance for Kinetic Analysis

Although the numeric calculations with the various types of means originally had been carried out only in order to test the fundamental equations, it seems to be worthwhile to look at the effect that is exercised by the type of mean on the values obtained for the various kinetic quantities of interest under the same external conditions (same value of the parameter b). Furthermore, inspection of these results might help in deciding which type of mean is really operative in experimental systems.

Clearly, the exponents α and β in the power laws (in the absence of chain transfer)

$$v_p = \text{const}(t)v_0^{\alpha} \tag{54}$$

$$\bar{P}_n = \text{const}'(t)v_0^{-\beta} \tag{55}$$

are independent of the type of mean chosen (this has already been demonstrated on comparing the geometric mean and the harmonic mean approximation;[5] details of calculations with different values of the quantity C, which is a measure of v_0, $v_0 \sim C^{-2}$, are omitted here for the sake of brevity), the only effect being that the numeric values of the constants depend on t, the parameter characterizing the type of mean. This is demonstrated in Figure 4, where $(\overline{k_t}/k_t^\circ)^{1/2}$ is plotted vs. $S_2^{(0)}$ $(=\bar{P}_n - 1)$ on a double-logarithmic scale for M_1 to M_6.[13] In principle, these constants behave as the kinetic chain length ν or the ratio $(\overline{k_t}/k_t^\circ)^{-1/2}$ at a given value of C. Thus, from experimental investigations based on eq 54 and 55 only the exponents α and β, which are connected with b by[6]

$$\alpha = (1 - b)/(2 - b) \tag{56}$$

$$\beta = 2/(2 - b) \tag{57}$$

might be determined, while, in the absence of any reference value for the numeric constant, there is no way of obtaining any information on the type of M from the absolute values of ν, v_p, or $\bar{P}_n$ experimentally. (Nevertheless, it is seen that, quite reasonably, the difference between S_1 and S_2, which

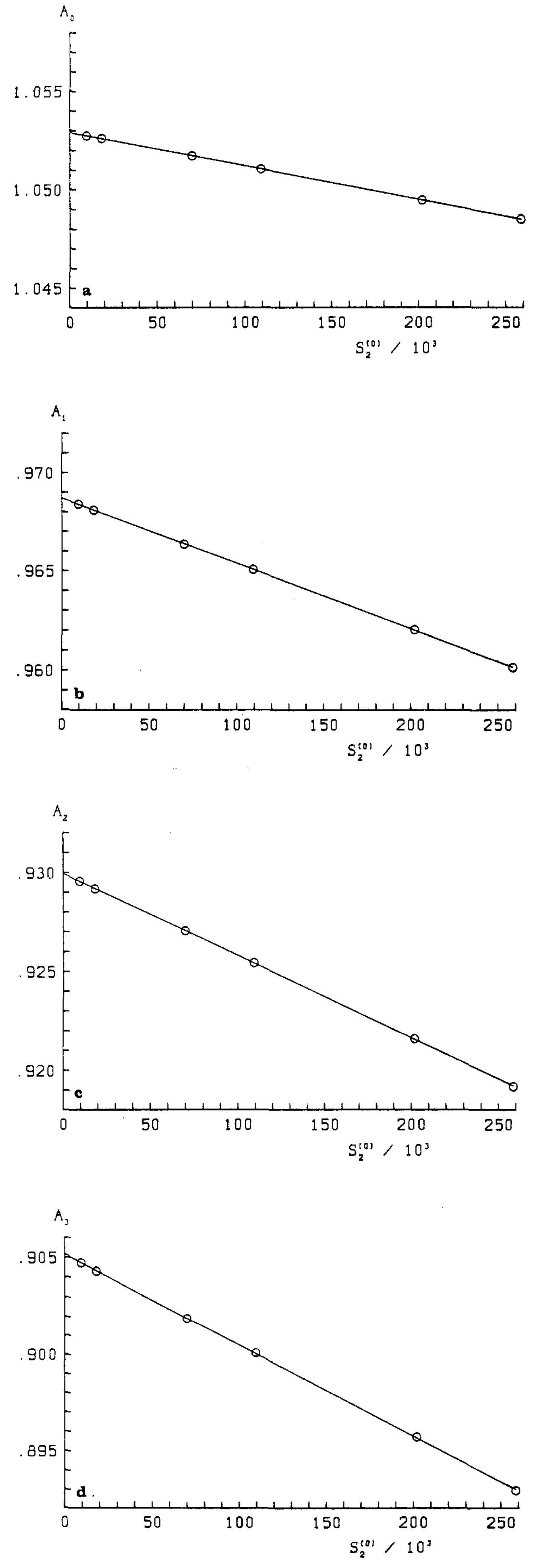

Figure 3. $A_k = (S_2^{(0)})^{b/2}S_1^{(k)}/S_2^{(k)}$ vs. $S_2^{(0)}/10^3$ for $C = 10^{-5}$ and for $D = 0$, $C/10$, $C/2$, C, $5C$, and $10C$ (geometric mean approximation, $b = 0.16$): (a) $k = 0$; (b) $k = 1$; (c) $k = 2$; (d) $k = 3$.

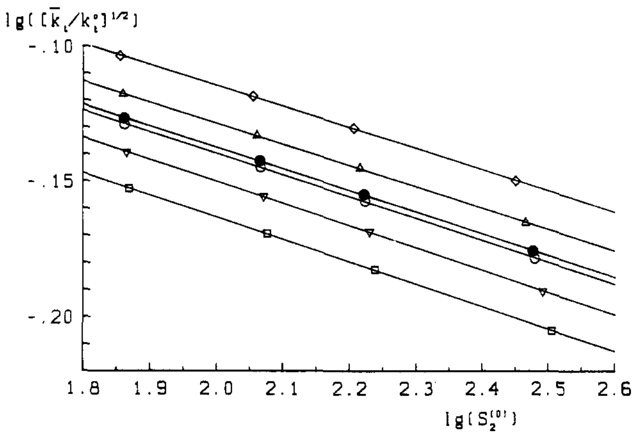

Figure 4. Double-logarithmic plots of $[\bar{k}_t/k_t^\circ]^{1/2}$ vs. $S_2^{(0)}$. Parameters (b, C, and D) and symbols as for Figure 1.

represents the primary qualitative indicator of chain length dependent termination, is largest for M_6 and smallest for M_1.) As a consequence, we have to direct our attention to those quantities that have the same functional dependence on v_0 ($\bar{x}_n$, $\bar{x}_w$, $\bar{x}_z$, $\bar{P}_n$, $\bar{P}_w$, and $\bar{P}_z$). For long chains their ratios, apart from being a function of the parameter b, then will depend only on the type of mean. Admittedly, as our data refer to comparatively short chains, the ratios obtained numerically might be slightly distorted; nevertheless, they will correctly reproduce the general trends. The following conclusions might be drawn from the data compiled in Table III:

(1) The ratio $\bar{x}_n/\bar{P}_n$ is always larger than unity and shows only little variation with the type of mean (from 1.087 for M_1 to 1.097 for M_6).

(2) $\bar{P}_w/\bar{P}_n$, the quantity that deviates most strongly from the value in classical free radical polymerization, where $\bar{P}_w/\bar{P}_n = 2$ for disproportionation ($\delta = 1$) and $\bar{P}_w/\bar{P}_n = 1.5$ for recombination ($\delta = 0$), varies only very slightly with the type of mean.

(3) On the other hand, $\bar{x}_w/\bar{x}_z$, which deviates much less from the ideal value of 2 (at least for the geometric mean normally used), is strongly dependent on the type of mean, with the deviation from 2 nearly vanishing for M_1.

(4) This difference in behavior between $\bar{P}_w/\bar{P}_n$ and $\bar{x}_w/\bar{x}_n$ is *not* transferred to the higher polydispersity ratios $\bar{P}_z/\bar{P}_w$ and $\bar{x}_z/\bar{x}_w$, which behave fairly equal and on passing from M_6 to M_1 fall from 1.585 to 1.51 ($\bar{x}_z/\bar{x}_w$) and 1.61 to 1.53 ($\bar{P}_z/\bar{P}_w$, $\delta = 1$). Again M_1 shows the smallest deviation from the ideal value of 1.50, which is characteristic of classical free radical polymerization.

Finally, we shall try to give an answer to the question of which quantity would offer the best prospects of assessing the type of mean M_i controlling the termination process. Unfortunately, $\bar{x}_w/\bar{x}_n$, which is the quantity varying strongest with the parameter t, defies experimental determination. Thus, as $\bar{P}_w/\bar{P}_n$ is highly sensitive to chain length dependence of termination but is only slightly influenced by the type of mean, it may be used rather to decide whether there *is* chain length dependence of termination or not but is more or less ineffective in providing any statement on M_i. As a consequence, one has to resort to $\bar{P}_z/\bar{P}_w$ as that experimentally accessible quantity containing the (relatively) highest level of information on the type of mean operative. Somewhat fortunately, it is exactly this quantity that is extremely well reproduced by the procedures developed in section IV-C even if the long-chain-limit equations (method A) are applied. However, as in reality the choice most probably is restricted to M_2, M_3, and M_4 only, discrimination between these three means would afford fractionations of such a high accuracy and reliability which the present experimental facilities might not be able to warrant. Furthermore, any other side reaction or disturbing parameter not considered here might introduce further difficulties. As a result of this analysis, it seems to be extremely difficult to work out a successful experimental route of determining M_i. Nevertheless, this route invariably will have to make use of the differences in the molecular weight distribution of the dead polymer which would be caused by the different means.

VI. Final Remarks

The fundamental equations (eq 22 and 23) developed in this paper prove to be helpful in providing universal relationships between kinetic quantities. Their knowledge reduces the problem of solving the kinetic scheme for any form of chain length dependence of k_t to the evaluation (either by closed calculation, if possible, or numerically) of the expression $(\bar{k}_t/k_t^\circ)^{1/2}P^{b/2}$, which is fairly constant for moderate values of the parameter b and varies only by a few percent on passing from its limiting value for predominant termination by disproportionation to its limiting value for predominant chain transfer. If both these limiting values are accessible, as is the case with the geometric mean approximation in the long-chain approximation, a fully exact solution can be provided. In all other cases, the (exact) numeric data obtained by iterating the chain length distribution can be reproduced with fair accuracy. Furthermore, due to the factorizability connected with the geometric mean approximation, in addition an exact treatment of a kinetic scheme involving termination by recombination is possible in this case.

References and Notes

(1) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Macromolecules*, preceding paper in this issue.
(2) Olaj, O. F.; Zifferer, G.; Gleixner, G. Preprints of "Makromolekulares Kolloquium", Freiburg/Brsg., Germany, March 4–6, 1982, pp 21–22.
(3) Zifferer, G. Doctoral Thesis, University of Vienna, 1982.
(4) Mahabadi, H. K. *Macromolecules* **1985**, *18*, 1319.
(5) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem.* **1986**, *187*, 977.
(6) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 773, 851.
(7) Olaj, O. F.; Zifferer, G.; Gleixner, G.; Stickler, M. *Eur. Polym. J.* **1986**, *22*, 585.
(8) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1972; Chapter 3, p 10.
(9) This name is inspired by the fact that the bimolecular rate constant of a diffusion-controlled reaction is proportional to the sum of the diffusion constants D_x and D_y of the two molecules involved. If these depend on chain length according to $D_x \sim x^{-t}$ and $D_y \sim y^{-t}$, respectively, neglecting any eventual chain length dependence of the collision diameter (which enters as another factor) would lead to a rate constant whose chain length dependence is characterized by an M_3-type of mean (see also ref 11). In addition, this type of mean is also presumed to apply to the reptation model of termination between large radicals at high conversions (Coyle, D. J.; Thulig, T. J.; Tirell, M. *Ind. Eng. Chem. Fundam.* **1985**, *24*, 343).
(10) Actually, for numerically solving the expression for the diffusion mean it is not necessary to evaluate the complete double sum in eq 10. S_1^2 in this case is obtained simply as the product of two single sums by an iteration process.
(11) Ito, K. *J. Polym. Sci., Part A-2* **1969**, *7*, 241; *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1991.
(12) Olaj, O. F.; Zifferer, G., in preparation.
(13) Actually, there are very small but noticeable deviations of the slopes from the theoretical value of $-b/2$ which are caused by the fact that the short-chain behavior is slightly dependent on the type of mean.

Lattice–Fluid Theory of Polymer Solutions

Constantinos G. Panayiotou

Department of Chemical Engineering, University of Thessaloniki, Thessaloniki, 54006, Greece.

Received May 2, 1986

ABSTRACT: A molecular theory of r-mer fluid mixtures is presented. It is based on the Sanchez–Lacombe lattice–fluid model for r-mer fluids and their mixtures. Each molecule is characterized by a constant number of segments in the pure state and in solution. A more general mixing rule is used for the close-packed volume per segment in the mixture and in the one-fluid approach. The number of contact sites is not considered constant for all types of segments, and, thus, surface area fractions are introduced in the formalism of the model. Experimental data on all basic thermodynamic quantities of mixing for poly(dimethylsiloxane), polyisobutylene, and natural rubber solutions are used to test the theory. Liquid–liquid phase equilibria are considered for polymer–polymer mixtures. For this case, the effect of the binary parameters is discussed. Extension of the theory to account for gas solubilities in polymeric liquids is also discussed. The theory is compared with the original Sanchez–Lacombe theory and Flory's equation-of-state theory of polymer solutions.

In recent years there has been a sustained interest toward the development and refinement of statisticomechanical theories of the liquid state.[1,2] The radial distribution function approach has proved a successful treatment of liquids formed by small molecules of nearly spherical force fields. For macromolecules, however, its applicability is limited and exact theoretical treatments remain elusive. Approximate treatments whose common starting point is the partition function formulation are commonly used as an alternative. In this respect, free-volume models for polymer solutions[3-7] have proved quite successful in explaining their thermodynamic behavior, including volume changes on mixing, the composition dependence of the Flory–Huggins χ interaction parameter, and the exhibition of lower critical solution temperatures by nonpolar polymer + nonpolar solvent mixtures as well as polymer + polymer mixtures. In these models the characteristics of the pure liquids, as manifested, for example, in their equations of state, are taken into account for the description of the thermodynamic behavior of their mixtures. From a quantitative standpoint, the success of these models is heavily based not only on the judicious choice of the binary parameters but also on the adequate description of pure component behavior.

The "cell" character of the so-called FPP (Flory–Patterson–Prigogine) theory[3-5] and the lack of any detailed

0024-9297/87/2220-0861$01.50/0