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KINETICS OF PSEUDOSTATIONARY FREE RADICAL POLYMERIZATION—I. A FIRST APPROACH*

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Abstract—A general analysis of pseudostationary polymerization kinetics in the absence of chain transfer is presented. In the course of the treatment, a set of "higher order" pseudostationary conditions is established and it proves to be extremely helpful in dealing with degrees of polymerization. It is found that, in the long chain limit, several relations (particularly that between the product of rate of polymerization and the weight-average degree of polymerization) are of full general validity and remain unaffected by the detailed conditions of (periodic) initiation. Furthermore, the additional broadening of the chain length distribution relative to stationary polymerization can be correlated in a simple manner with the dispersion of instantaneous radical concentrations R_t, $\overline{R_t^2}/(\overline{R_t})^2$.

INTRODUCTION

When a system that is polymerizable by a free radical mechanism is subjected to strictly periodically varying conditions of initiation, a so-called "pseudostationary" state will be established within some periods and it is characterized by a periodic time-profile of radical concentration (or instantaneous rate of polymerization) exhibiting the same period length as the initiating profile. From that point onwards, maxima or minima of the radical profile will be invariant with time. As a consequence we encounter a constant overall radical concentration and rate of polymerization (if regarded on a time scale much longer than the period length t_0) although the instantaneous values within the period may well vary. The same arguments, of course, apply to the rate of initiation v_i and the rate of termination v_t which have to equal each other on this large time scale in order to preserve pseudostationarity.

The most famous example of a pseudostationary system in the field of polymerization kinetics is produced by the so-called rotating sector technique first introduced by Melville [1] and most successfully applied in the benchmark investigations by Bartlett and Swain [2], Burnett and Melville [3], Matheson *et al.* [4], etc. Here the photo-initiation is periodically interrupted by interposing a rotating sectored shutter between the light source and the reaction vessel. From the dependence of the rate of polymerization (relative to the rate observed at full light intensity) on sector speed (or rather period length), the ratio k_p/k_t (k_p = rate constant of chain propagation, k_t = rate constant of bimolecular termination between polymer radicals) can be evaluated. Another example of a pseudostationary technique is the polymerization initiated by periodic laser flashes. This again yields k_p/k_t, here from the dependence of conversion per flash on period length (i.e. pulse separation) t_0 [5]. In order to resolve this ratio into its components, however, it is necessary to fall back upon the ratio k_p^2/k_t determined from truly stationary experiments. The situation is similar for the space-analogue of the rotating sector technique, the spatial intermittent polymerization (SIP-) reactor, introduced into polymerization kinetics by O'Driscoll and Mahabadi [6].

In fact, much effort has been made (e.g. in working out corrections) to establish the rotating sector method as a tool for evaluating reliable k_p/k_t-values. On the other hand, somewhat surprisingly, very little attention has been paid to the degree of polymerization of the polymers formed under pseudostationary conditions, neither experimentally nor theoretically; furthermore no systematic investigation of free radical polymerization under generalized pseudostationary conditions has been given although the subject should be of considerable interest. So, during a theoretical treatment of pulsed laser-initiated polymerization [7], we discovered that a relation of striking simplicity between the weight average degree of polymerization $\bar{P}_w$ and the rate of polymerization v_p in the absence of chain transfer, which is known from stationary polymerization,

$$v_p \bar{P}_w = (3 - \delta) k_p^2 M^2 / k_t \tag{1}$$

(where M is the monomer concentration and δ is the contribution of termination by disproportionation to overall termination) is valid also for pseudostationarity, with all other quantities characteristic of the experiment (laser flash intensity, pulse separation t_0, etc.) dropping out. The same equation was obtained during a theoretical analysis of molecular weights of polymers originating from rotating sector experiments and their distribution [8]. Admittedly, special simplified experimental conditions had been assumed in both derivations. Thus, a delta-pulse initiation was postulated in the first case and a

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*Dedicated to Professor H. Janeschitz-Kriegl, Johannes-Kepler University, Linz, Austria, on the occasion of his 65th birthday, remembering many pleasant hours spent together in scientific discussions and in playing chamber-music.

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constant rate of initiation during the light period in the second and no radical formation was assumed during the dark periods in both cases. Nevertheless, we felt that equation (1), which is valid also for true stationarity (continuous initiation) might be of quite general character and apply to arbitrary pseudostationary conditions, at least in the long chain limit and in the absence of chain transfer. This is the more noteworthy as the corresponding equation for the product $v_p\bar{P}_n$ under stationary conditions

$$v_p\bar{P}_n = \frac{2}{1+\delta} k_p^2 M^2/k_t \tag{2}$$

fails for pseudostationarity.

In view of the enormous importance which pseudostationary experiments appear to have for the evaluation of individual rate constants, some general analysis of their kinetic aspects appears to be desirable. Furthermore, as equation (1) proved to be extremely helpful in estimating k_p *and* k_t from one *single* pseudostationary experiment [7, 9, 10] (together with the direct evaluation of k_p and—if necessary—also δ from the molecular weight distribution of the polymer formed [11]) we decided to seek a derivation of equation (1) for arbitrary pseudostationary conditions in the absence of chain transfer.

KINETIC ANALYSIS

Preliminaries

We consider a period of length t_0 which we subdivide into n intervals of length $(k_pM)^{-1}$ (and to which we assign numbers from $i = 1$ to $i = n$) so that $t_0 = n(k_pM)^{-1}$, where n should be much larger than unity. $(k_pM)^{-1}$ is exactly that time which (on average) is necessary to increase the length of a growing chain by one monomeric unit. As a consequence the probability α_i that a growing chain of a certain length will further propagate in the i-th interval (and not terminate) which is defined by

$$\alpha_i = k_pM/(k_pM + k_t R_i), \tag{3}$$

can be correlated to the polymer radical concentration R_i at that moment. The initiation profile is defined by a set of r_i-values which represent the concentrations of primary radicals produced in the interval i. We assume quantitative transformation of primary radicals into radicals of unit degree of polymerization. Anticipating approximations ($\alpha_i \approx \alpha_{i+1}$; $\alpha_i \approx 1$) of the type to be introduced below the relationship between radical concentrations in successive intervals takes the form

$$R_{i+1} = (R_i + r_i)\alpha_{i+1} \approx R_i\alpha_i + r_i. \tag{4}$$

The condition of pseudostationarity implies that all the features prevailing in the i-th interval will be exactly recovered after each t_0, i.e. in the j-th interval, $j = n + i$, $j = 2n + i$, etc. In order to abbreviate the derivation, we shall partly resort to a formalism which has been developed to cope with the problem of chain length dependent termination in stationary polymerization [12, 13]. (The common factor between our *pseuodostationary* polymerization with chain length *independent* termination and *stationary* polymerization with chain length *dependent* termination is that the propagation probabilities in general are not the same for different degrees of propagation, the differences being due to the chain length itself in the latter case while they are caused by the different radical concentrations in the former.) This formalism enables us to represent the moments of the distribution of chain lengths x and the various averages of the degree of polymerization in terms of the k-th moments of the distribution of "living" i.e. non-terminated polymer chains defined by

$$S^{(k)} = \sum_{x=1}^{\infty} x^k \prod_{j=1}^{x} \alpha_j, \tag{5}$$

if termination is by disproportionation. The same principle holds also for the more complicated situation of termination by combination as in our present case the problem is greatly simplified by the fact that k_t itself is a constant so that the so-called factorizability condition applies without restriction.

Termination by disproportionation

Quite generally, the moments of the chain length distribution of a polymer initiated by monoradicals and terminated by disproportionation in a bimolecular reaction with other polymer radicals can be written as

$$m^{(k)} = \sum_{x=1}^{\infty} x^k(1-\alpha_x)\prod_{l=1}^{x-1}\alpha_l \tag{6}$$

where the indices x and l refer to the chain-length. Taking the differences and recalling that α_l and α_x can be identified with the propagation probabilities characteristic of the interval in which propagation should occur, we obtain for a polymer initiated in interval i

$$\begin{aligned}(m^{(2)})_i &= 1 + 3\alpha_{i+1} + 5\alpha_{i+1}\alpha_{i+2} + 7\alpha_{i+1}\alpha_{i+2}\alpha_{i+3} + \cdots \\ &= 1 + S_i^{(0)} + 2S_i^{(1)}, \end{aligned} \tag{7a}$$

$$\begin{aligned}(m^{(1)})_i &= 1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2} + \alpha_{i+1}\alpha_{i+2}\alpha_{i+3} + \cdots \\ &= 1 + S_i^{(0)} \end{aligned} \tag{7b}$$

$$(m^{(0)})_i = 1 \tag{7c}$$

where the second lines in equations (7a) and (7b) refer to the abbreviated representation according to equation (5).

In calculating the moments of the overall polymer formed in the whole period, we have to take the sums of the individual moments over i (from i = 1 to i = n) weighed with the probability of their occurrence, $r_i/\Sigma r_i$

$$m^{(k)} = \sum_{i=1}^{n} r_i(m^{(k)})_i \Big/ \sum_{i=1}^{n} r_i. \tag{8}$$

Replacement of r_i by R_i and R_{i+1} according to equation (4), recalling the periodic behaviour of R_i and r_i ($R_i = R_{n+i}$, $r_i = r_{n+i}$, $\alpha_i = \alpha_{n+i}$), we obtain the important relations

$$\begin{aligned}&\sum r_i(1 + 3\alpha_{i+1} + 5\alpha_{i+1}\alpha_{i+2} + \cdots) \\ &\qquad = \sum R_{i+1}(1 + 2\alpha_{i+1} + 2\alpha_{i+1}\alpha_{i+2} + \cdots),\end{aligned} \tag{8a}$$

$$\sum r_i(1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2} + \cdots) = \sum R_{i+1} = \sum R_i, \tag{8b}$$

$$\sum r_i = \sum R_i(1 - \alpha_i), \tag{8c}$$

all the outer summations to be carried from i = 1 to i = n while all the sums within parentheses go from i to infinity, the various α_i again being subject to periodic behaviour ($\alpha_i = \alpha_{i+n} = \alpha_{i+2n}$ etc.)

The polydispersity ratio $\bar{P}_w/\bar{P}_n$ then takes the form

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{m^{(2)}m^{(0)}}{[m^{(1)}]^2}$$

$$= \frac{\left[\sum R_{i+1}(1 + 2\alpha_{i+1} + 2\alpha_{i+1}\alpha_{i+2}\ldots)\right]\left[\sum R_i(1-\alpha_i)\right]}{\left(\sum R_i\right)^2}. \tag{9}$$

Now, neglecting unity in comparison with $1 + 2\alpha_{i+1} + 2\alpha_{i+1}\alpha_{i+2} + \cdots$ which is reasonable in the long-chain approximation (actually $1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2} + \cdots = S_i^{(0)}$ is the number-average degree of polymerization of a polymer initiated during the i-th interval [12, 13]) we may write

$$1 + 2\alpha_{i+1} + 2\alpha_{i+1}\alpha_{i+2} + \cdots$$
$$\approx 2(1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2} + \cdots) = 2(1 + S_i^{(0)})$$

and further assuming that

$$\sum R_{i+1}(1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2}\ldots)$$
$$\approx \sum R_i(1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2} + \cdots) \tag{10}$$

or equivalently

$$\sum R_{i+1} S_i^{(0)} \approx \sum R_i S_i^{(0)}, \tag{10a}$$

which means that the "phase difference" between the two factors is not important and above all is compensated on summation because of the cyclic character of the problem, the product in the numerator N of equation (9) can be treated in the following way.

(1) In the long-chain limit ($\alpha_i \approx 1$) where

$$\alpha_i \approx (k_p M - k_t R_i)/(k_p M), \tag{3a}$$

the rate of termination in the i-th interval can be approximated also by

$$(v_t)_i = k_t R_i^2 \approx R_i(1 - \alpha_i)k_p M, \tag{11}$$

so that

$$R_i(1 - \alpha_i) = k_t R_i^2/(k_p M). \tag{12}$$

Thus,

$$\sum R_i(1 - \alpha_i) = (k_t/(k_p M))\sum R_i^2$$
$$= n(k_t/(k_p M))\overline{R_i^2}. \tag{13}$$

(2) Proper back-elimination of $k_t/(k_p M)$ [$= R_i^{-1}(1 - \alpha_i)$ for arbitrary i] makes the individual radical concentrations drop out so that the numerator N of equation (9) finally reads

$$N = 2n\overline{R_i^2}\sum(1 + \alpha_{i+1} + \alpha_{i+1}\alpha_{i+2} + \cdots)$$
$$\times (1 - \alpha_i) = 2n^2\overline{R_i^2} \tag{14}$$

for periodic conditions.

As the denominator simply is $n^2(\overline{R_i})^2$, we end up with the simple result

$$\bar{P}_w/\bar{P}_n = 2\overline{R_i^2}/(\overline{R_i})^2. \tag{15}$$

It is straightforward to represent $\overline{R_i^2}$ and $\overline{R_i}$ by rate expressions. Thus,

$$\overline{R_i^2} = v_t/k_t \tag{16}$$

and

$$\overline{R_i} = v_p/(k_p M). \tag{17}$$

Substitution into equation (15) yields

$$\bar{P}_w/\bar{P}_n = 2(k_p M)^2 v_t/(k_t v_p^2). \tag{18}$$

Recalling that for termination by disproportionation

$$\bar{P}_n = v_p/v_t, \tag{19}$$

equation (1) is recovered for the case of $\delta = 1$.

Termination by combination

When treating this mode of termination, usually that situation is considered which is present at the moment of termination and the history of the two combining radical chains has to be traced back to the moments when the two independently growing radicals were created. In our scheme, however, more emphasis is given to the moment when chains are initiated (represented by the set of r_i-values). However, as Bamford *et al.* have shown [14], in the absence of chain transfer, monoradical initiation and termination by combination are equivalent to biradical initiation (without any topological constraint, of course) and termination by disproportionation. Although this argument is thought to be strictly valid for truly stationary polymerization only, it will hold true also for pseudostationary polymerization if a whole period is considered. Thus, due to the equivalence of whether coupling is on heads or tails, we can simply replace the fractions of polymer terminated by combination by the (hypothetical) fractions of polymer initiated by biradicals at some interval i and subject them to the general scheme of treating combination mentioned before [12, 13].

According to this general scheme, the moments of the chain length distribution of such a polymer (to which we assign bold face letters **m** in order to discriminate between them and those for disproportionation-terminated polymer) by analogy to equations (7a–c) may be represented in terms of the sums defined by equation (5)

$$(\mathbf{m}^{(2)})_i = 2 + 3S_i^{(0)} + 2S_i^{(1)} + (S_i^{(0)})^2, \tag{20a}$$

$$(\mathbf{m}^{(1)})_i = 1 + S_i^{(0)}, \tag{20b}$$

$$(\mathbf{m}^{(0)})_i = \tfrac{1}{2}, \tag{20c}$$

$(\mathbf{m}^{(2)})_i$ may be split into two parts, $(\mathbf{m}^{(2)})_{i,A}$ and $(\mathbf{m}^{(2)})_{i,B}$

$$(\mathbf{m}^{(2)})_{i,A} = 1 + S_i^{(0)} + 2S_i^{(1)} \tag{21a}$$

and

$$(\mathbf{m}^{(2)})_{i,B} = 1 + 2S_i^{(0)} + (S_i^{(0)})^2 = (1 + S_i^{(0)})^2. \tag{21b}$$

$(\mathbf{m}^{(0)})_i$, $(\mathbf{m}^{(1)})_i$ and $(\mathbf{m}^{(2)})_{i,A}$ equal the moments for polymer terminated by disproportionation (apart from the factor 1/2 in the zeroth moment) so that the same values as for disproportionation (again with a factor of 1/2 for the zeroth moment) are obtained when the moments are evaluated for the whole period after application of equation (4).

$$(\mathbf{m}^{(2)})_A = \sum r_i(1+S_i^{(0)}+2S_i^{(1)}) \approx \sum 2R_i(1+S_i^{(0)}), \tag{22a}$$

$$\mathbf{m}^{(1)} = \sum r_i(1+S_i^{(0)}) = \sum R_i \tag{22b}$$

$$\mathbf{m}^{(0)} = \tfrac{1}{2}\sum r_i = \tfrac{1}{2}\sum R_i(1-\alpha_i). \tag{22c}$$

Thus, the first constituent of $\overline{P}_w/\overline{P}_n$ for a polymer terminated by combination, $(\overline{P}_w/\overline{P}_n)_A$, which corresponds to the first part of $(\mathbf{m}^{(2)})_i$, is half the value of $\overline{P}_w/\overline{P}_n$ for a polymer terminated by disproportionation, which means, according to the treatment outlined in the preceding paragraph, that

$$\left(\frac{\overline{P}_w}{\overline{P}_n}\right)_A = \frac{(\mathbf{m}^{(2)})_A\mathbf{m}^{(0)}}{(\mathbf{m}^{(1)})^2} = \frac{\overline{R_i^2}}{(\overline{R_i})^2}. \tag{23a}$$

In dealing with the second contribution of the individual second moments, equation (21b), application of equation (4) leads to

$$\begin{aligned}(\mathbf{m}^{(2)})_B &= \sum r_i(1+S_i^{(0)})^2 \\ &= \sum R_i[(1+S_i^{(0)})^2 - S_i^{(0)}(1+S_{i+1}^{(0)})].\end{aligned} \tag{24}$$

Again, neglecting the difference between $S_i^{(0)}$ and $S_{i+1}^{(0)}$ in this summation over $i=1$ to $i=n$ considering periodicity, we obtain as a fair approximation

$$(\mathbf{m}^{(2)})_B \approx \sum R_i(1+S_i^{(0)}). \tag{25}$$

The "weight-average" degree of polymerization corresponding to this second contribution $(\mathbf{m}^{(2)})_B/\mathbf{m}^{(1)}$ then is simply

$$\frac{(\mathbf{m}^{(2)})_B}{\mathbf{m}^{(1)}} = \frac{\sum R_i(1+S_i^{(0)})}{\sum R_i}, \tag{26}$$

which in the long-chain limit can be identified with half the weight-average degree of polymerization of a polymer which would have been formed if the termination mode were disproportionation, see ratio of equations (8a) and (8b) together with equation (10). On the other hand, $\mathbf{m}^{(1)}/\mathbf{m}^{(0)}$ is double the number-average degree of polymerization of the polymer that would have formed with termination by disproportionation, see equations (8b) and (8c). Thus, with equation (15) we finally obtain for the second contribution to the polydispersity ratio $(\overline{P}_w/\overline{P}_n)_B$

$$\left(\frac{\overline{P}_w}{\overline{P}_n}\right)_B = \frac{(\mathbf{m}^{(2)})_B/\mathbf{m}^{(1)}}{\mathbf{m}^{(1)}/\mathbf{m}^{(0)}} = \frac{1}{2}\frac{\overline{R_i^2}}{(\overline{R_i})^2}. \tag{23b}$$

The overall polydispersity ratio then is given as the sum of the two contributions defined by equations (23a) and (23b)

$$\frac{\overline{P}_w}{\overline{P}_n} = \left(\frac{\overline{P}_w}{\overline{P}_n}\right)_A + \left(\frac{\overline{P}_w}{\overline{P}_n}\right)_B = \frac{3}{2}\frac{\overline{R_i^2}}{(\overline{R_i})^2}. \tag{27}$$

Subjecting this result to the procedure sketched in equations (15)–(18) and recalling that for termination by combination $\overline{P}_n = 2v_p/v_t$ leads to the recovery of equation (1) for $\delta = 0$.

As $\overline{P}_w$ is a linear function of δ [12, 13] (the mode of termination affects only the degree of polymerization but not the rate), the relation between rate of polymerization v_p and weight-average degree of polymerization $\overline{P}_w$ assumes the general form of equation (1) for $0 \leqslant \delta \leqslant 1$.

DISCUSSION

The foregoing section has produced results which deserve further consideration.

(1) Generalized conditions of pseudostationarity

Without any doubt, equations (8a–c) play a key part in the development. Not only do these equations transform summations over the initiation profile (r_i) into summations over the radical profile (R_i), they also lower the order of the moments appearing in the summations by one which—as a consequence—increases the tractability of the expressions. Thus, equation (8b) leads to an expression for the sum of radical concentrations which is free from any other quantities. Equation (8c), in its turn, which states the radical production to equal the radical consumption, both summed up over a full period, can be identified as the "condition of pseudostationarity" in its simplest form. By analogy, therefore, equation (8b) and (8c) must be considered to represent pseudostationarity conditions of higher order which are of particular general value in treating degrees of polymerization.

(2) Polydispersity

One of the most striking features by-passed in the course of this treatise are the findings contained in equations (15) and (27). According to these equations, the polydispersity ratio $(\overline{P}_w/\overline{P}_n)_{psst}$ in pseudostationary polymerization is given as the genuine polydispersity ratio characteristic of stationary polymerization, $(\overline{P}_w/\overline{P}_n)_{st}$, which in general form reads

$$\left(\frac{\overline{P}_w}{\overline{P}_n}\right)_{st} = \tfrac{1}{2}(3-\delta)(1+\delta), \tag{28}$$

multiplied by the factor $\overline{R_i^2}/(\overline{R_i})^2$

$$\begin{aligned}\left(\frac{\overline{P}_w}{\overline{P}_n}\right)_{psst} &= \left(\frac{\overline{P}_w}{\overline{P}_n}\right)_{st}\frac{\overline{R_i^2}}{(\overline{R_i})^2} \\ &= \frac{(3-\delta)(1+\delta)}{2}\frac{\overline{R_i^2}}{(\overline{R_i})^2}.\end{aligned} \tag{29}$$

This means that the mode of termination (disproportionation, combination, or any mixture of the two) has exactly the same influence on the polydispersity ratio in pseudostationary polymerization as already established for stationary experiments.

Apart from its plausible form, equation (29) provides a reasonable facility to estimate the non-homogeneity of radical concentration in pseudostationary polymerization experiments from polydispersity measurements [15].

(3) General validity of the equation for $v_p\overline{P}_w$

The development in fact distinguishes equation (1) as a fully universal relationship which in the long-chain limit and in the absence of chain transfer is valid for any arbitrary type of periodic initiation. As a consequence it will hold also under more realistic conditions than have been assumed in previous developments [7, 8]. Thus, neither radical formation during the dark period of a rotating sector experiment nor a time-lag in initiation following a laser-flash (which cannot be completely excluded) will invalidate equation (1) as long as the condition of periodicity is preserved.

There is a point in spotting the meaning of equation (1) in terms of the expressions contained in equations (8a–c) or (22a–c), respectively. Actually, when an expression for $\mathrm{v_p}$ is derived from equations (8b) and (17) using the general relation $\mathrm{n = t_0 k_p} M$

$$\mathrm{v_p = n^{-1} k_p} M \sum R_\mathrm{i} \tag{17a}$$

and (e.g. for disproportionation) $\mathrm{\bar{P}_w}$ is calculated by dividing equation (8a) by equation (8b) it is immediately clear that taking the product

$$\begin{aligned}\mathrm{v_p \bar{P}_w} &= \mathrm{k_p} M \frac{1}{\mathrm{n}} \sum R_\mathrm{i+1} (1 + 2\alpha_\mathrm{i+1} + 2\alpha_\mathrm{i+1}\alpha_\mathrm{i+2} + \cdots) \\ &= \mathrm{k_p} M \frac{1}{\mathrm{n}} \sum R_\mathrm{i+1} (1 + 2\mathrm{S_i^{(0)}}),\end{aligned} \tag{1a}$$

the expression for ΣR_i drops out. Comparing equation (1a) to equation (1) reveals that in the long-chain limit under pseudostationary conditions,

$$\frac{1}{\mathrm{n}} \sum R_\mathrm{i} \mathrm{S_i^{(0)}} = \mathrm{k_p} M / \mathrm{k_t}. \tag{30}$$

The same equation is also obtained if the equations for termination by combination, equations (22a–c), are treated in this way. Thus, the averaged product of instantaneous radical concentration R_i and $\mathrm{S_i^{(0)}}$ is a kinetically fixed quantity that is fully independent of the initiation profile. As $\mathrm{S_i^{(0)}}$ can be easily related to the number-average degree of the polymer which has been initiated in the interval i (which is characterized by the instantaneous radical concentration R_i)

$$(\mathrm{\bar{P}_n})_\mathrm{i} = \frac{2}{1 + \delta} \mathrm{S_i^{(0)}},$$

the generalized version of equation (30) will read

$$\frac{1}{\mathrm{n}} \sum R_\mathrm{i} (\mathrm{\bar{P}_n})_\mathrm{i} = \frac{1 + \delta}{2} \mathrm{k_p} M / \mathrm{k_t}. \tag{30a}$$

(4) Comparison of equations for $v_p \bar{P}_w$ and $v_p \bar{P}_n$

It seems worthwhile to consider the problem *why* equation (1) is insensitive to inhomogeneity of initiation while equation (2) is not. Starting with equation (29) and using the obvious relations for $\mathrm{\bar{P}_n}$

$$\mathrm{\bar{P}_n} = \frac{2}{1 + \delta} (\mathrm{v_p / v_i}) = \frac{2}{1 + \delta} \mathrm{k_p} M \overline{R_\mathrm{i}} \Big/ \left(\sum r_\mathrm{i} / \mathrm{t_0} \right) \tag{19a}$$

and for $\mathrm{v_p}$, equation (17),

$$\mathrm{v_p = k_p} M \overline{R_\mathrm{i}} \tag{17a}$$

leads to

$$\mathrm{v_p \bar{P}_w} = (3 - \delta) \left(\overline{R_\mathrm{i}^2} \Big/ \sum r_\mathrm{i} \right) (\mathrm{k_p} M)^2 \mathrm{t_0}. \tag{1b}$$

Thus, the expression for $\mathrm{v_p \bar{P}_w}$ contains the ratio $\overline{R_\mathrm{i}^2} / \Sigma r_\mathrm{i}$. As $\overline{R_\mathrm{i}^2}$ is related to the rate of termination $\mathrm{v_t = k_t} \overline{R_\mathrm{i}^2}$ and Σr_i is a measure of the rate of initiation $\mathrm{v_i} = \Sigma r_\mathrm{i} / \mathrm{t_0}$, it is clear that under the conditions of pseudostationarity (when $\mathrm{v_i = v_t}$) any influence of how initiation is effected in the polymerization system drops out. On the other hand, the corresponding relation for $\mathrm{v_p \bar{P}_n}$, as is obvious from equation (29), apart from a changed numerical factor depending on the mode of termination, contains $(\overline{R_\mathrm{i}})^2$ instead of $\overline{R_\mathrm{i}^2}$. As $\overline{R_\mathrm{i}}$ (or equivalently $\mathrm{v_p}$) are strongly influenced by the initiation profile, it is clear that no such universal relationship as established for $\mathrm{v_p \bar{P}_w}$ can exist for $\mathrm{v_p \bar{P}_n}$.

(5) Further universal relationships

In our treatment of laser-initiated pseudostationary polymerization, a quantity $(1 - \beta)$ has been defined which represents that fraction of the radicals created in a laser flash under pseudostationary conditions which is still unterminated when the subsequent flash arrives [5]. This quantity is of great importance as it enters into all expressions for polymerization rates, molecular weights and chain-length distributions [5, 7, 9, 11]. In particular, the expression for $\mathrm{v_p}$ could be represented as

$$(\mathrm{v_p} / M) \mathrm{t_0} = (\mathrm{k_p / k_t}) [-\ln(1 - \beta)]. \tag{31}$$

In the long chain limit, we can write the propagation probability α_i in the approximate form

$$\alpha_\mathrm{i} \approx \exp[-\mathrm{k_t} R_\mathrm{i} / (\mathrm{k_p} M)]. \tag{3a}$$

Passing a full period, therefore, means that the complete series of propagation probabilities will be operative. Due to the commutativity of factors in products, all radicals, in whichever interval i they were created, within the period length $\mathrm{t_0}$ will escape termination with an overall probability of

$$1 - \beta = \prod_{\mathrm{i=1}}^{\mathrm{n}} \alpha_\mathrm{i} = \exp\left(-\mathrm{k_t} \sum_{\mathrm{i=1}}^{\mathrm{n}} R_\mathrm{i} / (\mathrm{k_p} M) \right). \tag{32}$$

Substituting for ΣR_i from equation (17a) and subsequent rearrangement leads directly to equation (31). Thus, equation (31) represents another example of a universal relationship in pseudostationary polymerization. Its basic assertion is that the attenuation which radical species suffer during a full period is not only the same for all species irrespective of at which time they have been created but also that this attenuation law is always given by equation (31).

CONCLUSION

The present paper has proved the existence of some regularities and relationships which are valid in the long chain limit for *any* type of pseudostationary polymerization in the absence of chain transfer. Although these relations are of enormous importance for the evaluation of experiments carried out under pseudostationary conditions, we think that the relationships presented here constitute only a small part of the general information which is hidden behind the kinetic laws of pseudostationary polymerization. Thus, further research and systematic investigations in this field will be of great promise.

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