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The Kinetics of Free Radical Polymerization under Conditions of Diffusion-controlled Termination[1,2]

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The kinetic scheme for chain polymerization involving diffusion-controlled termination is worked out in detail. It is shown that of the two consecutive diffusion steps in a termination, the translational diffusion of the chain centers and the segmental diffusion of the active ends to within termination distance, the latter is always rate controlling. Two models for segmental diffusion are examined in detail. In one the segmental diffusion constant is assumed to be proportional to the chain diffusion constant. This "Ball and Chain Model" leads to reasonable average termination rate constants but predicts that the rate of polymerization varies with the 4/3 power of monomer concentration (M) and the 1/3 power of rate of initiation (R_i). In the second, physically more reasonable model it is assumed that segmental diffusion is characterized by a chain length dependence which is "Ball and Chain" for small chain lengths n and becomes independent of chain length as n exceeds N_L, where N_L is some characteristic segmental length associated with segmental diffusion. For values of $N_L < \nu$, the mean kinetic chain length, the rate law is nearly conventional with very reasonable values of mean termination constants. These are given by

$$k_t = \frac{4\,P_{AB}kT}{3\eta}\left[\frac{R_E}{x_0 N_L^{1/3}}\right]$$

where P_{AB} = a factor estimated crudely at 1/8 to correct the segmental diffusion constant for chain entanglement and restricted direction of approach; η = the macroscopic viscosity; R_E = the transition state separation of the ends. For $\eta = 0.5$ c.p.; $T = 300$°K.; $(R/x_0) = 1.4$; $N_L = 100$, $k_t = 1.1 \times 10^8$ l./mole sec. At low degrees of polymerization, ($\nu < N_L$) the rate of polymerization should show departures from conventional kinetics with R_P varying as some power of (M) slightly greater than unity and some power of R_i slightly less than 1/2. Techniques are developed for obtaining rate laws for polymerization systems with chain length dependent, termination constants in systems undergoing varying amounts of transfer.

Introduction

There has been indirect evidence for some time[4,5] that the termination reaction in free radical polymerizations is diffusion-controlled. Recently, direct measurements of the 2nd order termination rate[6,7] have shown that for methyl methacrylate the apparent termination rate constant is inversely proportional to the viscosity of the medium over a thousand-fold range of viscosity. Incomplete data indicate that the same results hold for styrene polymerization, and it is likely that this is true for most other monomers which have values of k_t, the second order termination rate constant, greater than or equal to k_t for methyl methacrylate.[8]

The inverse dependence of a rate constant on viscosity can be explained only in terms of a diffusion-controlled process, which is of course to be expected for radical–radical termination. However, in the case of long chain radicals, diffusion is not a simple phenomenon, and there are at least two kinds of diffusion which can play a role in bimolecular termination. In addition, we may expect that a diffusion-controlled reaction between radicals will show some dependence on the chain size of the reacting chains. In such an event the usual kinetic assumptions regarding the individual termination rate constants may not be valid, and the kinetic equations for polymerization will have to be reinvestigated.

In the present paper we shall derive an equation for the diffusion-controlled reaction of long chain radicals, present a simple model for the diffusion process and finally show how it is possible to obtain explicit solutions to the steady-state kinetic scheme when the termination rate constants are functions of the chain lengths of the reacting radicals.

I. The Diffusion Process.—In order for termination to occur between two free radical species, the active centers must diffuse to within a distance of separation of less than 4Å.[9] If there is no significant barrier to reaction of these centers, the rate will be controlled by the rates of diffusion.

In a solution dilute in radical species, the diffusion can be looked upon as a two-stage process. The first stage involves the translational diffusion of the centers of gravity of the two species to a distance sufficiently small that reaction can be completed without further change in this distance but merely by a segmental diffusion of the active centers of the chains to within the distance of about 3–4 Å. needed for termination. We can represent this dual diffusion by the kinetic scheme

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_D}{\rightleftarrows}} [\mathrm{A}\ldots\mathrm{B}] \qquad (1)$$

$$[\mathrm{A}\ldots\mathrm{B}] \xrightarrow[k_E]{} \mathrm{AB} \qquad (2)$$

where [A. . .B] represents a proximate A–B chain pair whose centers of gravity are at a distance R_{AB} apart. Using stationary state kinetics we find for the stationary concentration of [A. . .B]

$$[\mathrm{A}\ldots\mathrm{B}]_{ss} = \frac{k_D(\mathrm{A})(\mathrm{B})}{k_2 + k_E} \qquad (3)$$

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[4] I. Murphy and A. Wasserman, *J. Polymer Sci.*, **14**, 477 (1954).

[5] G. K. Oster, G. Oster and G. Prati, *J. Am. Chem. Soc.*, **79**, 595 (1957).

[6] S. W. Benson and A. M. North, *ibid.*, **81**, 1339 (1959).

[7] A. M. North and G. A. Reed, *Trans. Faraday Soc.*, **57**, 859 (1961).

[8] For butyl acrylate, diffusion control occurs only at viscosities in excess of 15 centipoises.

[9] This would apply to recombination. For disproportionation we would consider the abstractable atom as an active center.

while for the rate of termination

$$\frac{d(AB)}{dt} = k_E[A\ldots B]_{ss} \qquad (4)$$

$$= \frac{k_E k_D (A)(B)}{k_2 + k_E}$$

For the second order termination rate constant we find

$$k_t = \frac{k_E k_D}{k_2 + k_E} \qquad (5)$$

The rate constant k_D for formation of [A. . .B] pairs is given by the Smoluchowsky equation[10] for diffusion of particles into a sink of radius R_{AB}.

$$k_D = 4\pi D_{AB} R_{AB} = 4\pi(D_A + D_B)R_{AB} \qquad (6)$$

Here D_{AB}, the diffusion constant of A relative to B, is the sum of the translational diffusion constants of A and B. If we assume that [A. . .B] comprises all proximate pairs of chains whose centers of gravity are separated by a distance less than or equal to R_{AB}, then the equilibrium constant for the formation of such pairs, K_{AB} is given by[11]

$$K_{AB} = \frac{4}{3}\pi R_{AB}^3 \qquad (7)$$

Since $k_D/k_2 = K_{AB}$ this allows us to calculate k_2

$$k_2 = 3D_{AB}/R_{AB}^2 \qquad (8)$$

The rate constant k_E can be estimated by assuming that termination occurs within the proximate pair, by segmental diffusion of the active centers of A and B with an effective diffusion constant D_E. If again we apply the Smoluchowsky equation, we obtain

$$k_E = 4\pi D_E R_E C_E \qquad (9)$$

where C_E is the mean concentration of active centers in the proximate pair and R_E is the distance between the active centers at termination, presumably of the order of 3 to 4 Å. The mean concentration of active centers C_E, is just the reciprocal of the mean total volume of the proximate pair. The mean volume V_{AB} of the proximate pair can be estimated from our initial assumption that end-to-end coupling can take place between A and B without further motion of their centers of gravity. If the coupling corresponds to recombination, and we assume that the volume occupied by the chain links in the transition state resembles that in the final polymer chain AB, then the equivalent radius R_{AB} is given by the Random–Walk relation

$$R_{AB}^2 = R_A^2 + R_B^2 \qquad (10)$$

Thus since $C_E = 1/V_{AB}$ and $V_{AB} = \frac{4}{3}\pi R_{AB}^3$

$$C_E = \frac{3}{4\pi R_{AB}^3}, \quad k_E = \frac{3D_E R_E}{R_{AB}^3} \qquad (11)$$

Substituting all of these values back into equation 5 we find

$$k_t = \frac{4\pi D_E D_{AB} R_E R_{AB}}{D_{AB} R_{AB} + D_E R_E} \qquad (12)$$

For two limiting cases we can write

Case I: Slow segmental diffusion ($D_E R_E << D_{AB} R_{AB}$)

$$k_t \longrightarrow 4\pi D_E R_E \qquad (13)$$

Case II: Slow chain diffusion ($D_E R_E >> D_{AB} R_{AB}$

$$k_t \longrightarrow 4\pi D_{AB} R_{AB} \qquad (14)$$

In Case I we might expect to find D_E independent of chain length except when A or B is very small. In this case k_t for slow, end-controlled termination will not be very sensitive to chain length. However it is expected that D_E will vary inversely with viscosity and thus so will k_t.

A very special case of case I, which has been discussed briefly[5] as the Ball and Chain Model is one in which D_E is proportional to the translational diffusion constant D_{AB}. The Smoluchowsky equation then yields

Case 1A: Ball and Chain Model

$$k_t = 4\pi P_{AB} D_{AB} R_E \qquad (15)$$

where P_{AB} is a steric factor to take into account the fact that diffusion together of the active segments is inhibited, both by the excluded volume of the radical chains and by entanglement of the radical chains.

In Case II, where translational diffusion is rate limiting, we can use the Einstein–Stoke's relation between η the viscosity and D the diffusion constant

$$D = kT/6\pi\eta r \qquad (16)$$

This gives for k_t

$$k_t = \frac{2kT}{3\eta}(1/R_A + 1/R_B)R_{AB} \qquad (17)$$

Using equation 10 for R_{AB} this becomes

$$k_t = \frac{2kT}{3\eta}\left[\left(1 + \frac{R_A^2}{R_B^2}\right)^{1/2} + \left(1 + \frac{R_B^2}{R_A^2}\right)^{1/2}\right] \qquad (18)$$

and with the random walk result that $R_A^2 \propto N_A$ where N_A = the chain length of A

$$k_t = \frac{2kT}{3\eta}\left[\left(1 + \frac{N_A}{N_B}\right)^{1/2} + \left(1 + \frac{N_B}{N_A}\right)^{1/2}\right] \qquad (19)$$

$$= \frac{2kT}{3\eta} f(n) \qquad (20)$$

It will be noted that for Case II, equations 19 and 20 predict a very peculiar dependence of k_t on chain length. The function $f(n)$ has a minimum value of 2.83 for $N_A = N_B$ and approaches $(N_A/N_B)^{1/2}$ for $N_A >> N_B$. The case $N_B >> N_A$ is of course completely symmetrical. The implication of this result is that once the two radical chains come to within a hydrodynamic distance R_{AB} of each other, they will remain within this distance for a time sufficiently long that termination is certain to occur. While this seems possible when both A and B are long chain species, it does not seem so for the case that either A or B is very small. If for example A is very small while B is not, we should expect that most of the diffusing is done by A and $D_{AB} \rightarrow D_A$; $D_E \rightarrow P_{AB} D_A$. But since R_B is then $>> R_A > R_E$, we see that from our original equation 12

$$k_t \longrightarrow 4\pi P_{AB} D_A R_E \qquad (21)$$

which is a result identical to that obtained with the Ball and Chain Model (eq. 15). The alternative to this is to assume the implausible result that a small radical in the vicinity of a large one is unusually likely to find the reactive center of the large radical before separating.

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[10] M. Smoluchowsky, *Z. phys. Chem.*, **92**, 129 (1918).

[11] This is obtained by assuming no interactions between the chains in proximate pair position. The concentration of such proximate pairs then is given by the number of B chains per unit volume, whose centers lie within a sphere of radius R_{AB} centered on an A chain center.

It should be noted that the chain length dependence of f(n) is very small. In any polymerizing system the bulk of the radical population will have chain lengths within a factor of 2 of the mean chain length. Thus the general range of N_A/N_B will be from 0.5 to 2.0, while the extremes will be at 0.25 to 4. For $N_A/N_B = 0.5$ or 2.0; f(n) = 2.98, only 5% greater than its minimum value f(1), while for $N_A/N_B = 1/4$ or 4; f(n) = 3.35, only 18% larger than f(1). Even for the extreme range $N_A/N_B = 0.1$ or 10 f(10) = 4.35 which is only 50% greater than f(1).

In consequence of this small chain length dependence we can assume with little error that f(n) = f(1) and calculate k_t from equation 19. For $\eta = 0.5$ c.p. at 300°K. we find values of k_t of about 1×10^{10} liter/mole sec., independent of the nature of the monomer. This value is about 200 times too large compared to experimental results and leads to the erroneous prediction that all k_t should be identical.

The conclusion from the above observations is that chain diffusion cannot be the rate limiting process in termination. The corollary is that the slow diffusion step must be segmental diffusion. The implication of this in terms of our original scheme (equations 1,2) is that the reverse step (k_2) of separation of the centers of gravity of two proximate chain pairs is always faster than the segmental diffusion together of the active ends. This is a physically quite reasonable result which further implies that the proximate chain pairs [A. . .B] are always in equilibrium with (A) and (B). One also can show that the rate of chain growth during the proximate chain termination step is negligibly slow.

We thus have reduced the termination process to Case I. To solve this rigorously would require a quantitative model for the slow segmental motion of chains. Unfortunately, none is available so that one is reduced to making more or less reasonable guesses about the quantity D_E (equation 13).

Insofar as the chain length dependence of D_E is concerned, the Ball and Chain Model (Case IA) corresponds to the extreme case and might be expected to be valid only when N_A or N_B or both are small.

For the Ball and Chain Model, the use of the Einstein–Stokes relation leads to

$$k_t = \frac{2kT}{3\eta} P_{AB} R_E \left(\frac{1}{R_A} + \frac{1}{R_B}\right) \tag{22}$$

$$= \frac{2kT}{3\eta} P_{AB} R_E \, g(R) \tag{23}$$

The chain sensitivity of this rate constant, contained in the expression g(R) = $(1/R_A + 1/R_B)$, is the greatest of all the cases considered. It predicts for example that the chances of termination of a radical of chain length 10^3 are about 16 times greater with a radical of chain length 1 than by a radical of comparable size.

If we assume that R_A, the hydrodynamic radius of the polymer chain is proportional to $n_A^{1/2}$ then $R_A = x_0 n_A^{1/2}$ where x_0 is a constant of proportionality.[12] The value of k_t for the Ball and Chain Model then becomes

$$k_t = \frac{2kT}{3\eta} \frac{P_{AB} R_E}{x_0} \left(\frac{1}{n_A^{1/2}} + \frac{1}{n_B^{1/2}}\right) \tag{24}$$

As the chain length is increased one would expect to find that D_E must become independent of the length. This can be expressed empirically as $D_E = D_{EA} + D_{EB}$ with D_{EA} (or D_{EB}) given by

$$D_{EA} = D_{EA}^0 + D_E(R_A) \tag{25}$$

A simple function which satisfies these conditions is

$$D_{EA} = D_E^0 \left(\frac{1}{R_A} + \frac{1}{R_L}\right) \tag{26}$$

where R_L corresponds to the limiting value of the hydrodynamic radius at which the segmental mobility becomes independent of chain length; *i.e.* $D_{EA} \rightarrow D_E^0/R_L$ as $R_A \rightarrow \infty$.[13a] If we take D^0_E as P_{AB} times the Einstein–Stokes coefficient (equation 16), then Case I reduces to

$$k_t = \frac{4P_{AB}kT}{3\eta} \frac{R_E}{R_L} \left[1 + \frac{R_L}{2}\left(\frac{1}{R_A} + \frac{1}{R_B}\right)\right] \tag{27}$$

or, with $R_A = x_0 n_A^{1/2}$

$$k_t = \frac{4P_{AB}kT}{3\eta} \left(\frac{R_E}{x_0 n_L^{1/2}}\right) \left[1 + \frac{n_L^{1/2}}{2}\left(\frac{1}{N_A^{1/2}} + \frac{1}{N_B^{1/2}}\right)\right] \tag{28}$$

The chain length dependence of k_t is now very small if n_L is of the order of magnitude of 100.[13b] Thus with $n_L = 100$ the chain length dependent term in brackets changes from a high value of 4.2 with $N_A = N_B = 10$ to 2.8 at $N_A = N_B = 50$; 2.0 at $N_A = N_B = 100$; 1.4 at $N_A = N_B = 500$; 1.3 at $N_A = N_B = 1000$ and 1.01 at $N_A = N_B = 10{,}000$. In the usual range of polymerization conditions N_A, N_B run from about 100 to 1000, corresponding to a 35% decrease in k_t with increasing degree of polymerization. As we shall see later, equations 24 and 28 give quite reasonable values for the termination rate constants. It is now of interest to see how a chain-length dependent, termination rate constant can be incorporated into the kinetic scheme.

II. The Kinetic Equations with no Transfer.—For purposes of simplicity let us consider a free radical, chain polymerization in which transfer reactions are unimportant but in which termination is diffusion-controlled. The chain scheme will be (M is monomer)

$$\begin{array}{lll} \text{Initiation} & \text{M} \xrightarrow{R_i} \text{P}_1 & \\ \text{Propagation} & \text{P}_1 + \text{M} \xrightarrow{k_p} \text{P}_2 & \\ & \text{P}_n + \text{M} \xrightarrow{k_p} \text{P}_{n+1} & \\ \text{Termination} & \text{P}_n + \text{P}_m \xrightarrow{k_{tmn}} \text{stable products} & (29) \end{array}$$

R_i is the rate at which monomer is converted into the simplest radicals P_1, k_p is the rate of propagation which we have assumed independent of chain size[14] while k_{tmn} are the chain-length dependent, termination rate constants.

Applying stationary state kinetics to this scheme for the individual radicals we find

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[12] From the random walk approximation, $x_0 \sim 2.2$ Å. for styrene.

[13] (a) Intuitively one would guess that R_L corresponds to about 100 chain units. (b) Note that equation 28 reduces to 24 as $n_L \rightarrow \infty$.

[14] This seems quite reasonable since the experimental evidence is that the propagation step requires activation energy and is not diffusion controlled.

$$R_i = \sum_{n,m} k_{tnm}P_nP_m = P^2 \sum_{n,m} k_{tnm}x_nx_m \qquad (30)$$

where $P = \Sigma P_n$, the total concentration of radicals and $x_n = P_n/P$, the mole fraction of radicals of chain length n. For the individual radical concentrations we find

$$P_1 = x_1P = \frac{R_i}{k_pM + P\sum_m k_{t1m}x_m} \qquad (31)$$

and the set of equations

$$\frac{x_n}{x_{n-1}} = \frac{k_pM}{k_pM + P\sum_m k_{tnm}x_m} \qquad (32)$$

or

$$x_n = x_{n-1}\left(1 + \frac{P}{k_pM}\sum_m k_{tnm}x_m\right)^{-1} \qquad (33)$$

The rate of polymerization is given by R_P, the rate of loss of monomer

$$R_p = -\frac{\mathrm{d}M}{\mathrm{d}t} = k_pMP \qquad (34)$$

If we define a mean kinetic chain length ν as the number of monomer units polymerized per radical formed, then

$$\nu = \frac{R_p}{R_i} = \frac{k_pMP}{P^2\sum_{n,m} k_{tnm}x_nx_m} \qquad (35)$$

This definition of ν can be used to simplify the expressions for the mole fractions of radicals.

$$x_1 = \frac{1}{\nu}\left[1 + \frac{P^2}{R_p}\sum_m k_{t1m}x_m\right]^{-1} \qquad (36)$$

$$x_s = \frac{1}{\nu}\prod_{n=1}^{s}\left[1 + \frac{P^2}{R_p}\sum_m k_{tnm}x_m\right]^{-1} \qquad (37)$$

or substituting for $(P)^2$ from equation 30

$$x_1 = \frac{1}{\nu}\left[1 + \sum_m k_{t1m}x_m/\nu\sum_{n,m} k_{tnm}x_nx_m\right] \qquad (38)$$

$$x_s = \frac{1}{\nu}\prod_{n=1}^{s}\left[1 + \frac{\sum_m k_{tnm}x_m}{\nu\sum_{n,m} k_{tnm}x_nx_m}\right]^{-1} \qquad (39)$$

Let us now define a dimensionless parameter f_{nm} which will express the chain length dependence of the termination rate constants

$$f_{nm} = k_{tnm}/k_{t11} \qquad (40)$$

We define also the auxiliary quantities f_n and F

$$f_n = \langle f_{nm}\rangle = \sum_m f_{nm}x_m \qquad (41)$$

$$F = \langle f_n\rangle = \sum_n f_nx_n \qquad (42)$$

Equations 38 and 39 now become

$$x_1 = \frac{1}{\nu}(1 + f_1/\nu F)^{-1}\ x_s = \frac{1}{\nu}\prod_{n=1}^{s}(1 + f_1/\nu F)^{-1} \qquad (43)$$

or

$$\ln(x_1\nu) = -\ln(1 + f_1/\nu F) \qquad (44)$$

$$\ln(x_s\nu) = -\sum_{n=1}^{s}\ln\left(1 + \frac{f_n}{\nu F}\right) \qquad (45)$$

Now it can be shown that $f_n << \nu F$, when the chain length is great[15] so that it is permissible to expand the logarithms and taking only the first terms in the series we have

$$\ln(x_s\nu) = -\frac{\sum_{n=1}^{s} f_n}{\nu F} = -\phi_s/\nu F \qquad (46)$$

with $\phi_s = \sum_{n=1}^{s} f_n$.

The set of equations represented by equation 46 can in principle be solved for the mole fractions x_s if f_{nm} are known. However, the solution is extremely difficult and another approach is indicated. It may be observed that the mole fractions must satisfy the normalization condition; $\Sigma x_s = 1$. Applying this to equation 40 we find

$$\nu = \sum_s \exp(-\phi_s/\nu F) \qquad (47)$$

or where the chain length is sufficiently long to replace the sum by an integral

$$\nu = \int_0^\infty \exp(-\phi_s/\nu F)\mathrm{d}s \qquad (48)$$

This last equation defines an algebraic relation between the quantities γ and F which once solved completes the solution of the problem without the necessity for solving the system of equations 46.[16] Let us first note that the kinetic parameters of interest, P, R_p and ν can all be related explicitly to F

$$P = R_i^{1/2}/k_{t11}^{1/2}F^{1/2} \qquad (49)$$

$$R_p = k_pMP = k_pMR_i^{1/2}/k_{t11}^{1/2}F^{1/2} \qquad (50)$$

$$\nu = R_p/R_i = k_pM/R_i^{1/2}k_{t11}^{1/2}F^{1/2} \qquad (51)$$

If then we can obtain a numerical relation between ν and F, it can be introduced into equation 51 to solve for ν and F in terms of the kinetic parameters and so on for P and R_p and finally x_s.

The solution of equation 48 for an algebraic relation between ν and F cannot be done generally but only in particular cases where the function f_{nm} is known. In the Appendix we shall show how to obtain solutions of equation 48 in a number of simple cases.

III. The Kinetic Equations with Transfer.—When the growing radical chains can transfer their activity to species S we must add to the kinetic scheme (equations 29) these steps

Transfer $\quad \mathrm{P}^{\cdot}_n + \mathrm{S} \xrightarrow{k_f} \mathrm{P}_n + \mathrm{S}^{\cdot}$

Re-initiation $\quad \mathrm{S}^{\cdot} + \mathrm{M} \xrightarrow{k_{if}} \mathrm{M}^{\cdot}_1$

Termination $\quad \mathrm{S}^{\cdot} + \mathrm{P}^{\cdot}_n \xrightarrow{k_{tfn}} \mathrm{SP}_n$

in which we have assumed that transfer is independent of chain length. This is justified by the same arguments used for assuming propagation independent of chain length.

Applying the stationary state method we find for the stationary concentrations of S· and P·

$$\frac{S^{\cdot}}{P} = \frac{k_fS^{\cdot}}{k_{if}M + P\Sigma k_{tfm}x_m} \qquad (52)$$

and for P·

$$R_i = P^2\left[\Sigma k_{tmn}x_mx_n + \frac{k_fS\Sigma k_{tfm}x_m}{k_{if}M + P\Sigma k_{tfm}x_m}\right] \qquad (53)$$

To avoid a complex arithmetical problem we shall make the reasonable assumption that the

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[15] Note that when $f_{nm} = 1, f_n/\nu F = 1/\nu$ and $x_s = e^{-s\nu}/\nu$.

[16] The auxiliary equation defining F

$$F = \int\int f_{nm}x_nx_m\,\mathrm{d}n\,\mathrm{d}m$$
$$= \int\int f_{nm}\exp - [(\phi_n + \phi_m)/\nu]\,\mathrm{d}n\mathrm{d}m/\nu^2$$

is not independent of equation 48 but in particular cases can be shown to be derivable from it.

transferred radicals S˙ are much more likely to reinitiate chains by attack on monomer than they are to terminate chains.[17] We then can simplify equations 52 and 53 by neglecting $P \Sigma k_{\mathrm{tfm}} x_{\mathrm{m}} << k_{\mathrm{if}} M$. If in addition we assume that the rate of re-initiation of chains by S is much faster than the rate of transfer so that $S^{\cdot} << \mathrm{P}$ we have:

$$\frac{S^{\cdot}}{P} \sim \frac{k_{\mathrm{f}}(\mathrm{S})}{k_{\mathrm{if}}(\mathrm{M})} << 1 \tag{54}$$

$$R_1 \sim P^2 \Sigma k_{\mathrm{tmn}} x_{\mathrm{m}} x_{\mathrm{n}} \tag{55}$$

which is the same as the previous equation for R_{i} (eq. 30).

The transfer conditions now comprise a situation in which the transferred radical concentration S˙ is a small fraction of the total concentration of all radicals so that we can neglect their effect on termination processes. Effectively, each time transfer occurs, the new radical re-initiates and the net effect of the transfer is to decrease the molecular weight without changing the over-all rate of polymerization (neglecting the effect of k_{t}).

If we now define a transfer chain length ν_{f} as the number of moles of monomer polymerized per mole of transfer then

$$\nu_{\mathrm{f}} = \frac{R_{\mathrm{p}}}{R_{\mathrm{f}}} = \frac{k_{\mathrm{p}} M}{k_{\mathrm{f}} S} \tag{56}$$

Using the same procedure as before we find for the mole fractions of radicals

$$\ln x_{\mathrm{s}} = \ln\left(\frac{1}{\nu} + \frac{1}{\nu_{\mathrm{f}}}\right) - \frac{s}{\nu_{\mathrm{f}}} - \frac{\phi_{\mathrm{s}}}{\nu_{\mathrm{f}}} \tag{57}$$

where ϕ_{s} and F are given by equations 46 and 42. Again a solution for F in terms of ν and ν_{f} is possible and will give the values of R_{p}, ν and P (equations 49–51).

Discussion

The model of slow translational diffusion (Case II) leads to conventional kinetics. However, as noted earlier, the model cannot be correct so we turn to the slow segmental motion models. Of these the Ball and Chain Model (Case IA) yields an extreme dependence of k_{t} on chain length and leads to a rate law in disagreement with the usual expression (eq. A 11). This would make it difficult to compare numerical results for k_{t} were it not for the fact that the differences are small. We can make a simulated comparison in the two extreme cases of no transfer or excessive transfer. When transfer is negligible, the comparison is given by

$$k_{\mathrm{t}}^{1/2} = R_{\mathrm{i}}^{1/6} b^{2/3} k_{\mathrm{t11}}^{2/3} / M^{1/3} k_{\mathrm{p}}^{1/3} \tag{58}$$

k_{t} is again, the apparent termination constant. When we calculate k_{t11} at viscosities of $^1/_2$ cp. (27°) from equation 24, setting $R_{\mathrm{E}}/x_0 = 1.4$, we find that $k_{\mathrm{t11}} \sim 4.5 \times 10^9 P_{\mathrm{AB}}$ l./mole sec. In the factor P_{AB} we include the correction to the Smoluchowski equation which arises from the fact that the diffusion together of the active centers is blocked by neighboring groups as well as chain entanglement. A crude estimate of P_{AB} from geometrical consideration gives it a value of about $^1/_8$ for styrene and other vinyl monomers of comparable dimensions. This would make k_{t11} about 6×10^8 l./mole sec. for the Ball and Chain Model.

Inserting this value of k_{t11} into equation 58 and using some typical values of R_{i}, M and k_{p}, we obtain a value of $k_{\mathrm{t}} \sim 3 \times 10^8$ which is high by a factor of 3 over the value listed for k_{t} (styrene) under the same conditions. Similar calculations for methyl methacrylate yield $k_{\mathrm{t}} \sim 1.5 \times 10^8$ l./mole sec., which is again higher by about a factor of 6 than the reported values. This order of agreement is within the limits of accuracy of both the model used and the simulated comparison and may be considered as satisfactory agreement.

Under conditions where chain length is governed principally by transfer, the kinetics of the Ball and Chain Model are closer to that of the conventional treatment and the simulated comparison of k_{t} is (eq. A28)

$$k_{\mathrm{t}} = 2\pi^{1/2} \left(\frac{k_{\mathrm{f}} S}{k_{\mathrm{p}} M}\right)^{1/2} k_{\mathrm{t11}} \tag{59}$$

When $S \sim M$, the values of $k_f/\mathrm{k_p} \sim 10^{-5}$ so that $k_{\mathrm{t}} \sim 1.1 \times 10^{-2} k_{\mathrm{t11}} \sim 6 \times 10^6$ l./mole sec. This is lower by about a factor of 3 to 10 than the observed values for termination constants. However, the implications of the above numbers, when transfer is chain length determining,[18] are that the mean degree of polymerization is about 10^5. This would apply only to a very high molecular weight of the order of 10^7 and is not a typical situation. For a more typical situation with a mean degree of polymerization of about 400 (*i.e.*, $k_{\mathrm{p}} M / k_f S = 400$), the value of $k_{\mathrm{t}} \sim 1.1 \times 10^8$ l./mole sec., which is high by about a factor of three. Again the factor is within the range of uncertainty of both the assumptions of the model and the crudity of the method of comparison.

For the semi-empirical model (eq. 28), the calculation in the Appendix (eq. A20) shows that the value of F is very close to $(1 + n_{\mathrm{L}}^{1/2})^{-1}$ and only slightly dependent on the kinetic parameters so long as $n_{\mathrm{L}} < \nu$, which seems quite reasonable. The experimental termination constant is then approximately equal to $k_{\mathrm{t11}}/(1 + n_{\mathrm{L}}^{1/2})$, and from equation 28 we find using $\eta = 0.5$ c.p., $T = 300$°K., $R_{\mathrm{E}}/x_0 = 1.4$ that $k_{\mathrm{t}} = 1.1 \times 10^8$ l./mole sec. for $n_{\mathrm{L}} = 100$ and 2.5×10^8 for the low value of $n_{\mathrm{L}} = 20$. These values are within a factor of 3 of the experimental values for styrene and methyl methacrylate and can be considered in excellent agreement with the data.

The considerations in the present paper then would lead us to conclude that termination reactions between polymer radicals are diffusion controlled, the slow step being the segmental motion of the active end of the polymer chain and that the effective diffusion constant for this step becomes independent of chain length for some limiting chain length of the order of about 100. Under such conditions the termination constant is insensitive to radical chain length and the conventional polymerization kinetics are appropriate.

Appendix

The Effect of Chain-length dependent termination on polymerization kinetics. Case IA.

$$f_{\mathrm{mn}} = \frac{1}{2}\left(\frac{1}{n^{1/2}} + \frac{1}{m^{1/2}}\right);\ \text{no transfer} \tag{A1}$$

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[17] At the opposite extreme when S˙ > P and termination is predominantly by S, the kinetics become very simple.

[18] Note that the ratio $(k_{\mathrm{p}} M / k_{\mathrm{f}} S) = \nu_{\mathrm{f}}$ is the mean kinetic chain length under these conditions.

This corresponds to the Ball and Chain Model (eq. 24) Then (see equations 40–42)[19]

$$f_n = \frac{1}{2}\left(n^{-1/2} + \int_0^\infty x_m m^{-1/2}\,\mathrm{d}m\right) \qquad \text{(A2)}$$

$$F = \int_0^\infty x_m m^{-1/2}\,\mathrm{d}m \qquad \text{(A3)}$$

$$\phi_s = s^{1/2} + \frac{s}{2}\int_0^\infty x_m m^{-1/2}\,\mathrm{d}m \qquad \text{(A4)}$$

The normalization equation 48 becomes

$$1 = \int_0^\infty \exp\left(-\frac{s}{2\nu} - \frac{2s^{1/2}}{\nu F}\right)\frac{\mathrm{d}s}{\nu} = \int_0^\infty \exp\left(-\frac{r}{2} - \frac{2r^{1/2}}{b}\right)\mathrm{d}r \qquad \text{(A5)}$$

where $r = s/\nu$ and the dimensionless quantity $b = \nu^{1/2}F$. Equation A5 now can be solved for the value of b. The procedure is to convert it, by simple change of variables and integration by parts into the form

$$e^{-g^2} = 2\,g\,\Pi^{1/2}\,[1 - Erf(g)] \qquad \text{(A6)}$$

where $g = 2^{1/2}b$. This equation, involving the error function $Erf(g)$ and its derivatives, is tabulated for all values of g. It has only one root which is then determined numerically, $g = 0.43$. Thus we find

$$b = F\nu^{1/2} = 2^{1/2}/g = 3.29 \qquad \text{(A7)}$$

Substituting this into equations 49 to 51 we find

$$F = b^{4/3}k_{t11}^{1/3}R_i^{1/3}/k_p^{2/3}(M)^{2/3} \qquad \text{(A8)}$$

$$P = k_p^{1/3}M^{1/3}R_i^{1/3}/b^{2/3}k_{t11}^{2/3} \qquad \text{(A9)}$$

$$\nu = k_p^{4/3}M^{4/3}/b^{2/3}\,k_{t11}^{2/3}R_i^{2/3} \qquad \text{(A10)}$$

and for the rate of polymerization

$$R_p = k_p^{4/3}M^{4/3}R_i^{1/3}/b^{2/3}k_{t11}^{2/3} \qquad \text{(A11)}$$

As might have been anticipated from the model itself, the rate is of a higher order than first in monomer and a lower order than half in initiation rate.

Case I.—

$$f_{mn} = \frac{\left[1 + \frac{n_L^{1/2}}{2}(n_A^{-1/2} + n_B^{-1/2})\right]}{[1 + n_L^{1/2}]};\ \text{no transfer} \qquad \text{(A12)}$$

This corresponds to slow segmental diffusion (eq. 28) The same substitutions yield ($c = 1 + n_L^{1/2}$)

$$cf_n = 1 + \frac{n_L^{1/2}}{2}\left(n^{-1/2} + \int_0^\infty x_m\,m^{-1/2}\,\mathrm{d}m\right) \qquad \text{(A13)}$$

$$cF = 1 + n_L^{1/2}\int_0^\infty x_m\,m^{-1/2}\,\mathrm{d}m = 1 + ab \qquad \text{(A14)}$$

where

$$a = n_L^{1/2}/\nu^{1/2};\ b = \nu^{1/2}\int_0^\infty x_m\,m^{-1/2}\,\mathrm{d}m$$

$$c\phi_s = s\left(1 + \frac{ab}{2}\right) + n_L^{1/2}s^{1/2} \qquad \text{(A15)}$$

The normalization condition now becomes

$$1 = \int_0^\infty \exp\left\{-\frac{r}{2}\left(\frac{2 + ab}{1 + ab}\right) - \frac{r^{1/2}\,a}{(1 + ab)}\right\}\mathrm{d}r \qquad \text{(A16)}$$

A change of variable and integration by parts gives

$$\frac{be^{-p^2}}{4}\left(\frac{2 + ab}{1 + ab}\right)^{1/2} = \frac{\Pi^{1/2}}{2} - \int_0^p e^{-x^2}\,\mathrm{d}x \qquad \text{(A17)}$$

with $p^2 = a^2/(1 + ab)(2 + ab)$.

Equation A17 defines a relation between a and b which again can be solved numerically from tabulated functions of the error integral and its derivatives. Solution of this equation shows that $0.5 < b < 1.76$ with very weak dependence on a in this range. The result is that we can set

$$F \sim (1 + n_L^{1/2}/\nu^{1/2})/(1 + n_L^{1/2}) \qquad \text{(A18)}$$

Substituting for ν from equation 51 we find

$$F = \frac{1}{(1 + n_L^{1/2})}\,[1 + n_L^{1/2}d\,F^{1/4}] \qquad \text{(A19)}$$

with $d^2 = k_{t11}^{1/2}R_i^{1/2}/k_p\ M \sim 1/\nu$. Since $n_L^{1/2} > 1$, F will be small and the term in brackets in equation A19 is close to unity. Thus setting $F^{1/4} \sim (1 + n_L^{1/2})^{-1/4} \sim n_L^{-1/8}$

$$F \sim \frac{1}{(1 + n_L^{1/2})}\,[1 + n_L^{3/8}\,d] \qquad \text{(A20)}$$

and

$$R_p = \frac{k_pR_i^{1/2}(M)}{k_{t11}^{1/2}}\,\frac{(1 + n_L^{1/2})^{1/2}}{(1 + n_L^{3/8}\,d)^{1/2}} \qquad \text{(A21)}$$

and for $n_L^{3/8}d < 1$:

$$R_p \sim \frac{k_pR_i^{1/2}(M)}{k_{t11}^{1/2}}\,(1 + n_L^{1/2})^{1/2}\left[1 - \frac{n_L^{3/8}}{2}\,d\right] \qquad \text{(A22)}$$

Since $d \propto R_i^{1/4}/M^{1/2}$ we note that the departure of the rate from conventional kinetics is represented by the term in brackets. The effect is to give an over-all rate, R_p which varies as somewhat less than 1/2 order in R_i and somewhat greater than first order in (M).

Case IA (with transfer).—The normalization condition now leads to (eq. 57)

$$\ln x_s = \ln\left(\frac{1}{\nu} + \frac{1}{\nu_f}\right) - \left(\frac{s}{\nu_f} + \frac{s}{2\nu}\right) - \frac{2s^{1/2}}{\nu F} \qquad \text{(A23)}$$

Using the orthogonality relation for x_s we can write

$$\frac{\nu_f}{2(\nu + \nu_f)} = ge^{g^2}\,\pi^{1/2}\left[1 - \frac{2}{\pi^{1/2}}\int_0^g e^{-z^2}\,dz\right] \qquad \text{(A24)}$$

with the quantity g defined by

$$g^2 = \frac{2\nu_f}{\nu F^2\,(\nu_f + 2\nu)} \qquad \text{(A25)}$$

This defines a relation between g and ν_f and ν which we now can solve numerically. The LHS of eq. A24 varies between zero when $\nu >> \nu_f$ (*i.e.* large rates of transfer) and $^1/_2$ when $\nu << \nu_f$ (*i.e.* — little transfer). The RHS of eq. A24 varies monotonically from zero when $g = 0$ to unity as $g \rightarrow \infty$. A solution is possible only for values of g which make the RHS less than $^1/_2$, and by using the tables of error functions it can be shown that this corresponds to values of $g \leq 0.43$.[20] But for such small values g it is of permissible to expand the RHS as a power series in g and to a sufficient degree of accuracy we can take the first term, whereupon

$$\frac{\nu_f}{2(\nu + \nu_f)} \sim \pi^{1/2}\,g \qquad \text{(A26)}$$

or replacing g from equation A25 we have

$$F = \frac{1}{g}\left[\frac{2\nu_f}{\nu(\nu_f + 2\nu)}\right]^{1/2} = \left[\frac{8\pi(\nu + \nu_f)^2}{\nu\nu_f(2\nu + \nu_f)}\right]^{-1/2} \qquad \text{(A27)}$$

While it is possible to substitute for ν from equation 51 and obtain an explicit solution for F in terms of the rate parameters, it is more instructive to observe that equation A27 has two limits. In the first when there is very little transfer, $\nu_f >> \nu$, and $F \rightarrow (8\pi/\nu)^{1/2}$ which corresponds to our previous solution (equation A7), though not exactly.[21]

The second limit obtains when there is much transfer ($\nu_f << \nu$), when $F \rightarrow (4\nu/\nu_f)^{1/2}$. Substituting this latter result into the equation 50 leads to[22]

$$R_p = \frac{k_p^{5/4}M^{5/4}R_i^{1/2}}{2^{1/2}\pi^{1/4}k_f^{1/4}k_{t11}^{1/2}S^{1/4}} \qquad \text{(A28)}$$

If in particular the transfer agent S is the monomer, then the rate of polymerization is once again proportional to the first power of M. The dependence on initiation rate is normal, *i.e.*, half order.

We have found quite generally that explicit solutions of the kinetic equations are possible whenever k_{tmn} can be written as sums of terms involving m, n, or m/n raised to arbitrary powers. More complex functions such as equation 19 can be approximated quite well by such functions. Thus $f(n) = 0.82 + (n_B/n_A)^{1/2} + (n_A/n_B)^{1/2}$ fits equation 19 to within 3% over the entire range of interest, and the solution for this $f(n)$ follows quite readily the general method.[23] The inherent symmetry of $f(n)$ with respect to m and n make such approximations quite straightforward.

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[19] In all of the above we have replaced sums by integrals.

[20] Note that this maximum corresponds to the previous solution (eq. A6) in the absence of transfer).

[21] The next higher term in the series expansion of equation A27 leads to a correction factor to F of $1/[1 + 4\nu_f^2/\pi^2(\nu + \nu_f)^2)]$ which approaches 0.71 for $\nu_f >> \nu$.

[22] A simple solution for F which satisfies both limits precisely and follows equation A27 reasonably well is: $F = 3.3\ (\nu^{-1/2} + 1.06\ \nu_f^{-1/2})$.

[23] We have obtained the explicit solutions for this case but omit them for lack of particular interest.