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Kinetics of Emulsion Polymerization

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As a basis for understanding emulsion polymerization, the kinetics of free radical reactions in isolated loci is discussed subject to the condition that the free radicals are supplied to the loci from an external source. Three cases of interest are considered: that in which the average number of free radicals per locus is small compared with unity, that in which this number approximates one-half, and that in which the number is large. Of these three possibilities, the second, in which the free radicals per locus approximate one-half, is by far the most interesting as it explains in a satisfactory manner the characteristic features of styrene emulsion polymerization. For this case the average rate of reaction per locus is independent of the size of the locus, since this rate is simply one-half the rate

of polymerization of a single free radical. Thus the rate of emulsion polymerization, the concentration of monomer in the loci, and the number of loci present provide the information needed for calculating the chain propagation constant for the monomer.

A simplified treatment is given for approximating the number of reaction loci (polymer particles) produced in emulsion polymerization when the rate of polymerization per locus is constant (see case 2 above). The law obtained indicates that the number of particles should increase with the soap concentration ($3/5$ ths power) and with the rate of formation of free radicals ($2/5$ ths power), but should decrease with increasing rate of growth of the free radicals ($-2/5$ ths power).

INTRODUCTION

ONE of the most interesting characteristics of emulsion polymerization is the production of high molecular weight polymer with simultaneous rapid rate of reaction. The most plausible current attempts to explain this consist in attributing an abnormally low value to the rate of mutual termination of growing free radicals due to the high viscosity of the polymerization locus (i.e., the swollen polymer particles).¹ However, a more attractive explanation is offered by a consideration of the kinetics of free radical reactions in isolated loci when the free radicals originate in a medium outside of the loci of reaction, or are generated by reaction of substances which come from the outside medium.

Harkins² has recently discussed the locus of the emulsion polymerization reaction and the function of the various phases present. His discussion may be briefly reviewed as follows. During emulsion polymerization there are four phases which play an integral role in the over-all process. The water phase normally contains the "catalyst," or more properly, chain initiator; it is probable that the initial formation of free radicals takes place here. Dispersed in the water

phase are emulsified droplets of monomer; as long as these remain present, they serve to keep the other phases supplied with monomer. In the early stages of the reaction, soap micelles containing dissolved monomer are present; these serve as "generators" of polymer particles and they continue to serve this function until all the soap becomes adsorbed on the polymer-water interface produced by the polymerization. After polymerization has started, the fourth phase present consists of very small polymer particles which are swollen with monomer; these serve as the principal loci of polymerization.

Thus, the problem of the kinetics of emulsion polymerization is twofold. There is the problem of determining what factors govern the rate of polymerization in a single swollen polymer particle and also there is the problem of determining how many such polymer particles are formed. Part I of this discussion is concerned with the first, while Part II presents a simplified discussion of the factors determining the number of reaction loci produced in emulsion polymerization.

In Part I the rate of polymerization is discussed for three limiting cases in terms of the variables: rate of formation of free radicals, rate of escape of free radicals from reaction loci, rates of termination of free radicals in reaction loci and water solution, rate of polymerization of a

¹ J. H. Baxendale, M. G. Evans, and J. K. Kilham, *J. Pol. Sci.* **1**, 466 (1946); W. P. Hohenstein and H. Mark, *J. Pol. Sci.* **1**, 549 (1946).

² W. D. Harkins, *J. Chem. Phys.* **13**, 381 (1945); **14**, 47 (1946); and *J. Am. Chem. Soc.* **69**, 1428 (1947).

free radical in a reaction locus, size, and number of reaction loci (polymer particles).

Case 1 is that in which the number of free radicals per reaction locus is much less than unity. Under these conditions, if termination is chiefly in the water phase, the rate law obtained is similar to the oil phase law, but the initiation rate and termination constant are those for the water solution, also a new factor appears which is the ratio of free radicals in the reaction loci to those in the water phase. The rate, therefore, is independent of the size of the reaction loci. If termination is in the reaction loci, the law is identical with the oil phase law except that the termination constant is replaced by a quantity giving the probability of escape of a free radical from a reaction locus. Since this latter quantity does involve the interfacial area, the rate is dependent on the size of the reaction loci but not very greatly so.

Case 2 is that in which the number of free radicals per reaction locus approximates one-half. This is the case of outstanding interest, since its existence is responsible for the extraordinarily high rates of polymerization and high molecular weights obtainable by emulsion polymerization. The rate law is remarkably simple since it involves only the rate of polymerization of a free radical and the number of reaction loci present. This simplicity makes it possible to determine the chain propagation constants of polymerizing monomers by studying their rates of emulsion polymerization.

Case 3 covers the situation when the number of free radicals per reaction locus is large. The rate law obtained is exactly equivalent to the oil phase law, and hence does not depend on the size of the reaction loci.

PART I. FREE RADICAL REACTION IN ISOLATED LOCI

Consider a system consisting of 1 cc of an external medium (water solution) having suspended in it N isolated reaction loci (polymer particles), each of which has a volume v and an interfacial area a . Suppose that free radicals are initiated only in the external medium, then let the rate of entrance of free radicals into a single locus be

$$dn/dt = \rho'/N,$$

where ρ' is the over-all rate of entrance into all the N loci.

Having once entered a locus, suppose that a free radical continues to cause polymerization until its activity is destroyed or transferred out of the locus. Let the rate of transfer out of a locus be given by

$$dn/dt = -k_0a(n/v),$$

where k_0 is a specific rate constant for the event, n/v is the concentration of free radicals in a locus, and a is the interfacial area through which the transfer takes place. Suppose that destruction of free radicals takes place only by mutual termination so that the rate of destruction in a given locus is given by

$$dn/dt = -2k_in[(n-1)/v],$$

where the factor of 2 arises from the fact that two free radicals are destroyed for each event of termination, k_t is the mutual termination specific reaction rate constant, and $(n-1)/v$ is the concentration of free radicals with which any of the n free radicals in a locus can react.

If these three events be the only ones which need be considered in determining the numbers of free radicals in the various reaction loci, then the $N_0, N_1, N_2 \dots N_n \dots$ reaction loci containing 0, 1, 2, $\dots n \dots$ free radicals, respectively, will be related by the steady-state condition:

$$\begin{aligned} N_{n-1}(\rho'/N) + N_{n+1}k_0a((n+1)/v) \\ + N_{n+2}k_t[(n+2)(n+1)/v] \\ = N_n\{\rho'/N + k_0a(n/v) + k_in[(n-1)/v]\}. \end{aligned} \quad (1)$$

This equation states that the rate of formation of reaction loci characterized by containing n free radicals is just equal to the rate of disappearance of these loci.

Rather than obtaining a general solution of this recursion formula, which would appear to be difficult, a discussion is given of three limiting cases which are of interest.

Case 1. Number of Free Radicals per Particle Small Compared with Unity

If the free radicals have a high enough probability of being transferred out of a particle, then at any time only a small number of the particles will have free radicals in them. This condition

will be fulfilled when

$$\rho'/N \ll k_0 a/v.$$

Then of the various relations given by Eq. (1), it is only necessary to consider the first which approaches

$$N_1 k_0 a/v = N_0 \rho'/N.$$

But since

$$N_0 \cong N, \quad N_1 \cong \rho'v/k_0 a.$$

The number of free radicals in polymer particles is also very nearly equal to N_1 , so if the rate of polymerization per free radical is $k_p(M)$ where k_p is the propagation constant and (M) is the monomer concentration in the particle, then the over-all rate of polymerization per cc of external medium (water solution) will be

$$dM/dt = k_p(M)(\rho'v/k_0 a). \quad (2)$$

An obvious alternative form for writing this equation is

$$dM/dt = k_p(M) V_p c_p, \quad (2a)$$

where V_p is the total volume of the polymer particles in 1 cc of water solution and c_p is the average concentration of free radicals in the particles.

Now termination of the free radicals may take place in either the water phase or the polymer particles. If termination is in the water phase, the rate law governing their disappearance may be written

$$dn/dt = -2k_t(c_w)^2,$$

where k_t is the termination constant and c_w is the concentration of free radicals in the water phase. When a steady state is attained, this rate will be equal to ρ , the rate of formation of free radicals per cc of water phase; thus

$$\rho = 2k_t(c_w)^2. \quad (3)$$

Under these conditions of rapid exchange of free radicals between water phase and polymer particles it is useful to use a partition coefficient, α , defined by

$$\alpha = c_p/c_w. \quad (4)$$

Then from Eqs. (2a), (3), and (4)

$$dM/dt = k_p(M) V_p \alpha (\rho/2k_t)^{1/2}. \quad (5)$$

Another quantity of interest is the average polymerizing lifetime of a free radical, which is a

measure of the initiator efficiency. The average lifetime, τ_p , of a free radical in polymer particles is equal to the number of free radicals in polymer particles divided by the rate at which they are terminated or

$$\tau_p = [V_p c_p / 2k_t(c_w)^2] = (V_p \alpha / 2k_t c_w).$$

From Eq. (3) this becomes

$$\tau_p = [V_p \alpha / (2k_t \rho)^{1/2}]. \quad (6)$$

Thus under these conditions the rate of polymerization and initiator efficiency do not depend on the size of the polymer particles but only on their total volume.

If termination takes place in the polymer particles and if these particles are so small that termination takes place very rapidly every time two free radicals are in the same particle, then the rate of termination is simply two times the rate at which free radicals enter the polymer particles which already contain a free radical or

$$dn/dt = -2(\rho'/N)N_1 = -2[(\rho')^2/N](v/k_0 a). \quad (7)$$

Equating this to the rate of formation of free radicals, ρ , to obtain the steady state condition, solving for ρ' and substituting in Eq. (2) gives

$$dM/dt = k_p(M)(V_p \rho / 2k_0 a)^{1/2}. \quad (8)$$

The mean polymerizing lifetime is approximately N_1 divided by the rate of termination; so from Eq. (7),

$$\tau_p = N/2\rho' = (V_p / 2k_0 a \rho)^{1/2}. \quad (9)$$

To know which of the two terminations discussed will apply, it is necessary to make an assumption concerning the relationship between c_w and ρ'/N . The simplest assumption to make is that the rate of entrance of free radicals into a particle is just that given by the rate of diffusion of molecules from an infinite medium of concentration c_w into a particle of radius, r , having zero concentration of the molecules, this rate is

$$\rho'/N = 4\pi D r c_w,$$

where D is the diffusion constant of the molecules through the water phase. Then the rate of termination in the polymer particles will be given by Eq. (7) to be

$$dn/dt = -2N(4\pi D r c_w)^2(v/k_0 a).$$

If this is small compared with the rate of termination in the water phase, Eq. (3), then the water phase termination will apply. Thus water phase termination predominates when

$$k_t \gg V_p(4\pi D^2/k_0).$$

Case 2. Number of Free Radicals per Polymer Particle Approximately Equal to 0.5

Suppose that there is no readily available mechanism by which the activity of a free radical in a polymer particle can be transferred again to the water phase, then having once entered a polymer particle a free radical must remain there until another one comes in to terminate it. If, in addition, the probability of mutual termination of two free radicals in the same particle is large enough so that the average time necessary for them to terminate is small compared with the average time interval between successive entrances of free radicals into a particle, then the very simple situation exists in which approximately one-half the particles contain a single free radical and the other half contain none. This is much the most interesting case and is the one which appears to apply to the emulsion polymerization of styrene under normal conditions. The requirements for this case can be stated as

$$k_0(a/v) \ll \rho'/N < k_t/v. \quad (10)$$

In view of the importance of this case, a solution will be given to a higher approximation than the simple limiting law; however, this will be done only for the condition in which $k_0=0$ (this is probably closely approached in many unregulated polymerizations). Neglecting terms involving k_0 , Eq. (1) becomes

$$N_{n-1}(\rho'/N) + N_{n+2}k_t[(n+2)(n+1)/v] = N_n\{(\rho'/N) + k_t n[(n-1)/v]\}. \quad (11)$$

For convenience, the quantity β may be defined as

$$\beta = k_t N / v \rho',$$

(from (10) $\beta > 1$) then Eq. (11) may be written

$$N_{n-1} + N_{n+2}\beta(n+2)(n+1) = N_n[1 + \beta n(n-1)]. \quad (12)$$

It is shown in Appendix I that a satisfactory approximation for this recursion formula when

$\beta > 1$ is

$$N_{n-1}/N_n = 1 + \beta n(n-1). \quad (13)$$

From Eq. (12) when $n=0$

$$N_2 = N_0/2\beta.$$

When $n=1$

$$N_0 + 3 \times 2 N_3 \beta = N_1.$$

But N_3 can be related approximately to N_2 by Eq. (13) so

$$N_3 = [N_0/2\beta(1+6\beta)],$$

and

$$N_1 = N_0(4+6\beta)/(1+6\beta).$$

This could be continued to obtain any degree of approximation desired.

So far as the rate of polymerization is concerned, the important thing is the total number of free radicals present in polymer particles; this is given by

$$n_T = 1N_1 + 2N_2 + 3N_3 + \cdots nN_n \cdots,$$

while the total number of particles is

$$N = N_0 + N_1 + N_2 + N_3 + \cdots N_n \cdots.$$

From these relations and those given above, the total number of free radicals can be expressed as the series

$$n_T = (N/2)(1 + 1/\beta - 1/3\beta^2 + \cdots). \quad (14)$$

Thus, if β is sufficiently large, the total number of free radicals present will be very nearly equal to one-half the number of polymer particles.

Under these conditions, the rate of polymerization per cc of water solution is given by the remarkably simple expression

$$dM/dt = k_p(M)N/2. \quad (15)$$

The mean polymerizing lifetime, τ_p , will be $N/2\rho'$. Under normal polymerization conditions, some semiquantitative considerations indicate that practically every free radical produced will enter polymer particles; hence $\rho' = \rho$ and

$$\tau_p = N/2\rho. \quad (16)$$

The characteristic features of emulsion polymerization can now be easily interpreted. It is seen from Eq. (14) that the number of polymerizing free radicals will be nearly equal to half the number of particles. Since it is possible to have a large number of particles present (compared

with the concentration of free radicals normally present in oil phase polymerization), the fast rate of polymerization naturally follows. Also from Eq. (16) the average lifetime of a free radical increases with increase in number of particles; thus it is possible to have high rates of polymerization with simultaneous high molecular weights in emulsion polymerizations.

It may be pointed out that when the conditions characterizing this case are fulfilled, determinations of the over-all rate of polymerization, number of polymer particles, and concentration of monomer in the particles provide the data necessary to calculate the chain propagation constant by Eq. (15).

Case 3. Number of Free Radicals per Polymer Particle Large Compared With Unity

This situation will prevail when

$$\rho'/N \gg k_t/v.$$

This case is not of as much interest as case 2, but in view of its possible application to some "bead polymerizations," a brief discussion will be given.

For most purposes, it is not necessary to have the detailed knowledge of the distribution of free radicals which would be provided by a solution of the recursion formula (1). It will suffice to write down directly the steady-state condition as

$$\rho'/N = 2k_t(n^2/v). \quad (17)$$

This assumes that the system can be approximated by one in which all the particles contain the same number, n , of free radicals. This is, no doubt, a good approximation if n is large enough. Solving Eq. (17) for n gives

$$n = (v\rho'/2k_tN)^{1/2}.$$

So the over-all rate of polymerization per cc of water solution will be

$$dM/dt = k_p(M)(V_p\rho'/2k_t)^{1/2}, \quad (18)$$

and the polymerizing lifetime of a free radical will be

$$\tau_p = (V_p/2k_t\rho')^{1/2}. \quad (19)$$

If the exposed interfacial surface is large enough so that practically every free radical produced

enters the particles, then $\rho' = \rho$, the rate of production of free radicals per cc of water phase. Then there will be no advantage in having a large number of very small particles as the rate and lifetime will depend only on the total volume of polymer particles. This will simply be an oil phase type of polymerization in suspended particles which are supplied with free radicals from the water phase. If a substantial fraction of the free radicals are terminated in the water phase, then the system is an inherently inefficient one.

Regarding the relationships between the three cases discussed, it is evidently possible, under suitable conditions, to go progressively from one case to the next by increasing the rate of formation of free radicals. However, for case 2 two conditions must be fulfilled; i.e.,

$$k_0(a/v) \ll (\rho'/N) < (k_t/v),$$

so, obviously, for this case to be obtained, k_0a must be much smaller than k_t . If this condition is not fulfilled, then progressive increase in the rate of formation of free radicals will cause a transition from case 1 to case 3 without ever realizing case 2.

PART II. NUMBER OF POLYMER PARTICLES

The process considered in this development is based on the ideas originated by Harkins² regarding the formation of polymer particles by soap micelles. It is considered that originally most of the soap present is in the form of micelles containing dissolved monomer. When a free radical from the surrounding water phase enters a micelle, it initiates polymerization of the monomer in the micelle. When this polymerization starts, monomer from the surrounding medium diffuses into the polymerizing region until shortly this region is no longer identified as a micelle, but is now considered a growing polymer particle and is subject to the considerations given in Part I. As the area of the polymer particles increases because of growth and formation of new ones, the particles adsorb more and more soap from the surrounding micelles until a time is reached at which no soap remains in the micellar form. After this time, the soap is no longer effective in forming new particles.

To make the problem as simple as possible,

the soap dissolved in the water without forming micelles and the soap adsorbed on the emulsified monomer may be neglected; ordinarily this soap will represent only a small fraction of the total present.² Thus, if S is the total amount of soap associated with one cc of water phase, it will consist of S_m grams in micellar form and S_p grams adsorbed on polymer particles so that

$$S = S_m + S_p. \quad (20)$$

Also for simplicity, it will be assumed that the interfacial area, a_s , occupied by a gram of soap is the same in soap micelles as on polymer particles, so long as micelles are present. This is probably not true but is a good enough approximation for the present discussion. So if A , A_m , and A_p are the total interfacial area, area of micelles, and area of polymer particles, respectively,

$$A/S = A_m/S_m = A_p/S_p = a_s.$$

Now the question arises as to how effective a given interfacial area is in collecting free radicals from the solution. If the ordinary laws of diffusion hold, as they probably do in this case, then a given interfacial area on a very small particle will be more effective in collecting free radicals than the same area on a large particle (i.e., the number entering a particle will be proportional to the radius; hence, the number entering a given area will be inversely proportional to the radius). This introduces some difficult complications into the problem. However, one can solve the problem of the number of particles produced for two idealized situations which should give, respectively, more and fewer particles than the actual situation. Fortunately, the results obtained do not differ greatly so it is thus possible to approximate fairly closely the actual situation, without having to discuss the size distribution of particles.

The simplest idealized situation is that in which the very small micelles capture all the free radicals being generated as long as micelles are still present. Obviously, this will give too many particles, since actually some of the free radicals will enter polymer particles. If ρ is the rate of formation of free radicals per cc of water solution, the rate of formation of new particles, dN/dt , is assumed equal to ρ and constant as long as

micelles are present. So

$$dN/dt = \rho. \quad (21)$$

To obtain the total number of particles formed, Eq. (21) must be integrated to the time t_1 at which the total area of the polymer particles, A_p , is just equal to the total area of the soap, $a_s S$.

The area of the polymer particles is the summation of the areas for all the particles produced from zero time to the time considered. To obtain the area at time t of a particle which was formed at time τ , it is necessary to know the law governing the rate of growth of a particle. For case 2 discussed in Part I, the rate of polymerization of a particle is a constant, independent of the size of the particle or of the rate of entrance of free radicals. Now if the ratio of monomer to polymer in the particle remains constant during the period in which new particles are being formed, the rate of increase in volume of a particle will be a constant which may be called μ , so if v is the volume of a particle

$$dv/dt = \mu.$$

Thus the volume, $v_{\tau, t}$, at time t of a particle formed at time τ is

$$v_{\tau, t} = \mu(t - \tau).$$

Assuming a spherical particle, the area, $a_{\tau, t}$, of this particle at time t is

$$a_{\tau, t} = [(4\pi)^{1/3} 3\mu(t - \tau)]^2. \quad (22)$$

For convenience make the substitution

$$\theta = [(4\pi)^{1/3} 3\mu]^2. \quad (23)$$

Then Eq. (22) becomes

$$a_{\tau, t} = \theta(t - \tau)^2. \quad (24)$$

The total area, A_p , of all the particles present at time t is given by the integration

$$A_p = \rho \theta \int_0^t (t - \tau)^2 d\tau, \quad (25)$$

which gives

$$A_p = (3/5) \rho \theta t^{5/3}.$$

At time $t = t_1$, when the soap micelles disappear, $A_p = a_s S$ so

$$t_1 = (5a_s S / 3\rho\theta)^{3/5}$$

and the total number of particles is

$$N = \rho t_1 = \rho^{2/5} (5a_s S / 3\theta)^{3/5} = 0.53 (\rho/\mu)^{2/5} (a_s S)^{3/5}. \quad (26)$$

The other idealized situation is that in which a given interfacial area always has the same effectiveness in collecting free radicals regardless of the size of the particle on which it is situated. This will give too few particles since a given interfacial area on the very small micelles will be more effective than the same area on the larger polymer particles. (The diffusion current of free radicals through unit area of interface should be inversely proportional to the radius.) For this situation, the rate of formation of particles is given by

$$dN/dt = \rho A_m / A, \quad (21a)$$

instead of by Eq. (21). Substituting from Eq. (20) gives

$$dN/dt = \rho(1 - A_p/a_s S). \quad (27)$$

The number of particles formed in the interval $d\tau$ at time τ may be expressed as $(dN/d\tau)d\tau$, and the area of one of these particles at some time, t , after τ is given by Eq. (24), so the total area at time t of all particles formed up to t is

$$A_p = \theta \int_0^t (t-\tau)^{1/3} (dN/d\tau) d\tau. \quad (25a)$$

Thus Eq. (27) may be written

$$dN/dt = \rho - (\rho\theta/a_s S) \int_0^t (t-\tau)^{1/3} (dN/d\tau) d\tau. \quad (28)$$

This integral equation is a form of Volterra's equation of the second kind³ which may be written

$$\phi(x) = f(x) + \lambda \int_0^x K(x, z) \phi(z) dz.$$

The solution of this is given by the infinite series

$$\phi(x) = \sum_{n=0}^{\infty} \lambda^n \phi_n(x),$$

where

$$\phi_0(x) = f(x) \quad \text{and} \quad \phi_n(x) = \int_0^x K(x, z) \phi_{n-1}(z) dz.$$

Applying this to Eq. (28), the desired solution

³ H. Margenau and G. M. Murphy, *Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 506.

may be expressed by the infinite series

$$\frac{dN}{dt} = \rho \sum_{n=0}^{\infty} \frac{y^n}{\Gamma(1+n5/3)}, \quad (29)$$

where

$$y = - \frac{(4\pi)^{1/3} 3^{2/3} \Gamma(5/3) \rho \mu^{2/3} t^{5/3}}{a_s S}.$$

Combination of the numerical constants gives

$$y = - \frac{4.36 \rho \mu^{2/3} t^{5/3}}{a_s S}. \quad (30)$$

By using a method of successive approximation, the value, y_1 , of y which gives $dN/dt = 0$ in Eq. (29) is found to be

$$y_1 = -2.13.$$

Thus the time t_1 at which the soap micelles disappear and after which no new particles are formed by them is (Eq. (30))

$$t_1 = \left(\frac{2.13 a_s S}{4.36 \rho \mu^{2/3}} \right)^{3/5} = \frac{0.650}{\mu^{2/5}} \left(\frac{a_s S}{\rho} \right)^{3/5}.$$

Now for temporary convenience let

$$\xi = (4.36 \rho \mu^{1/3} / a_s S),$$

so that (Eq. 30)

$$y = -\xi t^{5/3}.$$

Then the first few terms of Eq. (29), which are the only ones of importance, may be written out as

$$\frac{dN}{dt} = \rho \left(1 - \frac{\xi t^{5/3}}{\Gamma(8/3)} + \frac{\xi^2 t^{10/3}}{\Gamma(13/3)} - \frac{\xi^3 t^{15/3}}{\Gamma(18/3)} + \frac{\xi^4 t^{20/3}}{\Gamma(23/3)} - \dots \right).$$

To get the total number of particles produced by a given amount of soap, this may be integrated from $t=0$ to $t=t_1$, the time at which the soap micelles disappear. Carrying out term by term integration and substituting the limits gives

$$N = \rho t_1 \left(1 - \frac{3}{8} \frac{\xi t_1^{5/3}}{\Gamma(8/3)} + \frac{3}{13} \frac{\xi^2 t_1^{10/3}}{\Gamma(13/3)} - \frac{3}{18} \frac{\xi^3 t_1^{15/3}}{\Gamma(18/3)} + \frac{3}{23} \frac{\xi^4 t_1^{20/3}}{\Gamma(23/3)} - \dots \right),$$

or

$$N = 0.650 \left(\frac{\rho}{\mu} \right)^{2/5} (a_s S)^{3/5} \left(1 + \frac{3y_1}{8\Gamma(8/3)} + \frac{3(y_1)^2}{13\Gamma(13/3)} + \frac{3(y_1)^3}{18\Gamma(18/3)} + \frac{3(y_1)^4}{23\Gamma(23/3)} + \dots \right) \quad (26a)$$

$$= 0.370 (\rho/\mu)^{2/5} (a_s S)^{3/5}.$$

This is identical with Eq. (26) except for the value of the numerical constant, and the constants are not greatly different. The actual situation should lie between that represented by Eqs. (26) and (26a). Thus

$$N = k(\rho/\mu)^{2/5} (a_s S)^{3/5},$$

where $0.37 < k < 0.53$. The application of this to experimental data will be discussed in a future paper.

APPENDIX I

Approximate Solution of Recursion Formula For No Transfer of Free Radical from Polymer Particle to Water Phase

For convenience, make the substitutions

$$x = N_{n-1}/N_n, \quad x_1 = N_n/N_{n+1}, \quad x_2 = N_{n+1}/N_{n+2},$$

then the recursion formula (12) may be written

$$x = 1 + \beta n(n-1) - (1/x_1 x_2) \beta (n+2)(n+1). \quad (A1)$$

It is immediately evident that if x remains less than unity by a finite amount as $n \rightarrow \infty$ then the series $\sum_{n=0}^{\infty} N_n$ diverges and is therefore a physically unsatisfactory condition.

To examine the situation when $x \rightarrow 1$ as $n \rightarrow \infty$ consider the ratio of the free radicals in the N_{n+2} particles containing $n+2$ free radicals each to those in the N_n particles containing n free radicals each. This ratio, from Eq. (A1) is

$$\frac{(n+2)N_{n+2}}{nN_n} = \frac{n-1}{n+1} - \frac{x-1}{\beta n(n+1)}. \quad (A2)$$

Making the substitution

$$n' = n/2,$$

so that n' will now give the number of the term in the series

$$S = N_1 + 3N_3 + 5N_5 + \dots (2n'-1)N_{2n'-1}. \quad (A3)$$

The ratio expressed by (A2) now becomes

$$\frac{(n+2)N_{n+2}}{nN_n} = 1 - \frac{1}{n'} + \frac{1}{n'(2n'+1)} \left[1 - \frac{x-1}{2\beta} \right], \quad (A4)$$

which is the ratio of successive terms in the series of Eq. (A3). This is now in the form

$$a_{n+1}/a_n = 1 - \mu/n + \omega_n/n^k,$$

where $k > 1$ and $|\omega_n|$ is finite. The series $\sum_{n=r}^{\infty} a_n$ has been shown⁴ to diverge if $\mu \leq 1$. Therefore, the series in Eq. (A3) diverges so the condition $x \rightarrow 1$ as $n \rightarrow \infty$ is physically unacceptable.

The one remaining possibility is for x to remain greater than unity by a finite amount as $n \rightarrow \infty$. To examine this, it is convenient to rewrite Eq. (A1) in the form

$$x = 1 + \beta n(n-1) \left[1 - \frac{1}{x_1 x_2} \frac{(n+2)(n+1)}{n(n-1)} \right]. \quad (A5)$$

Since $x > 1$ as $n \rightarrow \infty$, then x_1 and x_2 must also remain greater than unity. Thus the term in brackets in Eq. (A5) must remain greater than zero. But since the multiplier, $\beta n(n-1)$, may become indefinitely large x , x_1 and x_2 will all become indefinitely large as $n \rightarrow \infty$. Thus the bracketed term will approach unity and the approximation

$$x \rightarrow 1 + \beta n(n-1), \quad (A6)$$

will be very good for large values of n ; also it will remain a good approximation for small values of n if β is large enough.

⁴ Frank and v. Mises, *Die Differential- und Integralgleichungen der Mechanik und Physik* (Friedrich Vieweg und Sohn Aktien-Gesellschaft, Braunschweig, 1930), p. 197.