

## Kinetics of Emulsion Polymerization

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### Synopsis

The quantitative theory of free radical mechanisms in emulsion polymerizations is re-examined. It is suggested that existing descriptions are not entirely consistent with physically realizable situations. The proposed modifications result in a closer resemblance to homogeneous systems. Explicit expressions for the distribution of radicals are also given. The importance of interphase transfer is emphasized.

A kinetic description of emulsion polymerizations must take into account the fact that the termination step involves a finite and usually quite small number of radical pairs in each latex particle. As a consequence, the usual rate equations in terms of macroscopic variables must be replaced by a probabilistic analysis. Such analyses have been provided by Stockmayer<sup>1</sup> and by Haward.<sup>2</sup> It is the purpose of this communication to extend the theory by presenting explicit expressions for the distributions of radical populations and to demonstrate that the solutions obtained by these authors, although mathematically correct, are physically unacceptable for small but finite rates of radical desorption.

The problem at hand is to predict the stationary distribution of growing molecules in a latex particle resulting from a zero-order absorption from the aqueous phase or intraparticle initiation, a first-order desorption or chain-stopping transfer, and a second-order termination reaction. For systems in which radicals appear singly one can follow Stockmayer and equate the rate of change of the probability of  $n$ -fold occupancy  $P_n$  to the net contribution of the three mechanisms. In the absence of time dependence a simpler, but equivalent, procedure is to set equal to zero the net flux of system points between states  $n$  and  $n + 1$ . The resulting recurrence relation is

$$k_d P_n = [k_a + (n/vk_t)](n + 1)P_{n+1} + (k_t/v)(n + 1)(n + 2)P_{n+2} \quad (1)$$

where the  $k$ 's are the rate constants, in molecular units, for the three mechanisms listed in the same order above and  $v$  represents the volume of the particle. The appearance of a second-order instead of third-order difference equation is analogous to the integration of the diffusion equation when applied to a steady state, one-dimensional problem.

Whatever the starting point our objective is most easily attained in

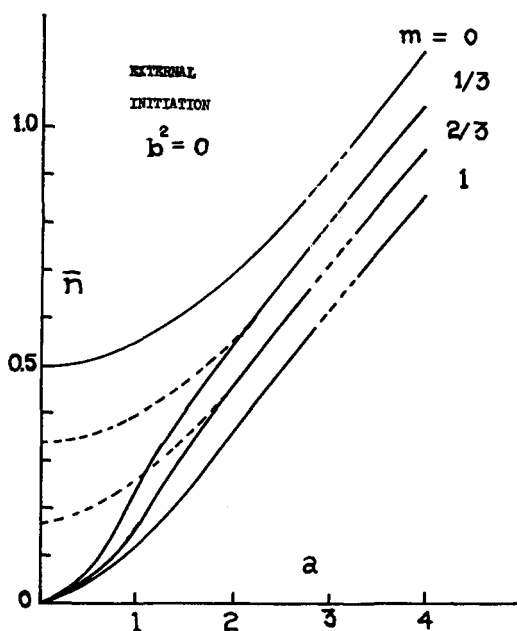


Fig. 1. Average radical population: (—) this work; (--) data of Stockmayer.<sup>1</sup>

terms of a generating function which satisfies a second-order differential equation having the general solution:

$$P = \sum_0^{\infty} P_n s^n = (1+s)^{(1-m)/2} \left\{ AI_{1-m} \left[ a \left( \frac{1+s}{2} \right)^{1/2} \right] + BI_{m-1} \left[ a \left( \frac{1+s}{2} \right)^{1/2} \right] \right\} \quad (2)$$

in which  $m = k_d v / k_t$ ,  $a = 2(2k_d v / k_t)^{1/2}$ , and  $I$  denotes the modified Bessel function of the first kind.

For integral values of  $n$  the two solutions are identical and no ambiguity arises. If desorption predominates, that is  $m > 1$ , the first solution diverges at  $s = -1$ , implying the existence of negative  $P_n$ . As a result of arguments such as these Stockmayer set  $A = 0$  in this region and apparently by means of similar reasoning concluded that  $B = 0$  for  $0 < m < 1$ . That the latter result is not the case can be demonstrated by inspection of the explicit formulae for the probabilities. Differentiation of the expression (2) and application of well known relations between the Bessel functions<sup>3</sup> lead to the inversion:

$$P_n = (a^2/8)^{n/2} (1/n!) [AI_{1-m-n}(a2^{-1/2}) + BI_{m-1+n}(a2^{-1/2})] \quad (3)$$

The acceptable distribution can be determined by examination of the asymptotic behavior for large  $n$ , namely:

$$P_n \sim (a^2/8)^{(1-m)/2} (1/n!) \{ (A/\pi)(n+m-2)! \sin(n+m-1) + [B(a^2/8)^{m-1+n}/(m-1+n)!] \} \quad (4)$$

The first term is clearly the dominant one in this limit and inasmuch as it alternates in sign must be rejected entirely. The normalized distribution valid for all values of  $m$  is thus given by

$$P_n = a^2 2^{(m-1-3n)/2} I_{m-1+n}(a 2^{-1/2}) / n! I_{m-1}(a) \quad (5)$$

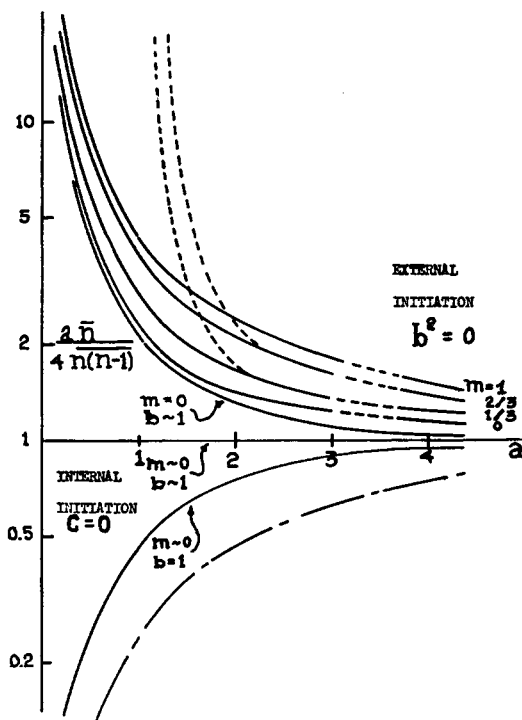


Fig. 2. Relative molecular weight: (—) this work; (--) data of Stockmayer;<sup>1</sup> (- -) data of Haward.<sup>2</sup>

In order to evaluate the molecular weight of the polymer and the conversion of monomer it is necessary to know the average populations of singlets and radical pairs. These values can be obtained from the moments of the distribution as

$$\bar{n} = \frac{\partial P}{\partial s} \Big|_{s=1} = a I_m(a) / 4 I_{m-1}(a)$$

$$(1/2) \overline{n(n-1)} = (1/2) \frac{\partial^2 P}{\partial s^2} \Big|_{s=1} = a^2 I_{m+1}(a) / 32 I_{m-1}(a) \quad (6)$$

In Figures 1 and 2 are plotted  $\bar{n}$  and the ratio  $a\bar{n}/4n(n-1)$  as functions of the parameter  $a$ . The second curve is effectively that of molecular weight against square root of initiation rate.

For many applications both  $a$  and  $m$  take on values much less than one. The following approximations then become valid:

$$\begin{aligned} \bar{n} &\sim k_a/(k_d + 2k_a) \\ \frac{\bar{n}}{n(n-1)} &\sim k_a v \bar{n}/k_t \end{aligned} \quad (7)$$

Should the loss of radicals to the aqueous phase be negligible,  $\bar{n} = 1/2$ , the limiting case originally treated by Smith and Ewart.<sup>4</sup>

In a second problem considered by Haward the radicals are created in pairs within the emulsified droplets and the first order loss constant is negligible. A solution is readily obtained according to which only even numbers of active centers per particle are possible. One may justifiably entertain doubts about such a literal interpretation of the model. In fact, Haward suggests a number of mechanisms which if operative to the slightest degree could transform this stochastic process on the even integers to an analogous one for which  $n = 1, 3$ , etc. It might even appear plausible that even and odd radical populations would be equally probable. Fortunately it is not necessary to rely on such intuitive arguments. The stable solution may be found by allowing for a finite but small value of  $k_d$  and thus including the Haward model within the framework of a more general treatment.

Accordingly we will look for the distribution which satisfies the stationary relation:

$$a^2(P_n + P_{n-1})/16 = (m+n)(n+1)P_{n+1} + (n+1)(n+2)P_{n+2} \quad (8)$$

the variables having the same significance as before. The additional term involving particles containing  $n-1$  radicals refers to the initiation process which transforms these states to those of occupancy  $n+1$ . The generating function defined by eq. (2) must satisfy the differential equation:

$$a^2 P/16 = [m/(1+s)](\partial P/\partial s) + (\partial^2 P/\partial s^2) \quad (9)$$

The general solution is easily obtained in terms of Bessel functions as

$$P = (1+s)^{(1-m)/2} \{ AI_{(1-m)/2}[a(1+s)/4] + BI_{(m-1)/2}[a(1+s)/4] \} \quad (10)$$

Proceeding as outlined above the coefficients are found to be

$$\begin{aligned} P_n &= \frac{1}{n!} \sum_{l=0}^{1/2(n-r)} \binom{1/2(n-r)}{l} \binom{l-1}{l}^{m/2} l! (-2)^l (a/4)^{n-l} \dots \\ &\quad [AI_{1/2(1-m)-l-r}(a/4) + BI_{l+r-1/2(1-m)}(a/4)] \end{aligned} \quad (11)$$

where  $\binom{r}{l}$  denotes the binomial factor and  $r = 0$  for even values of  $n$ ;  $r = 1$  for odd ones. Investigation of the behavior of this expression for large  $n$  reveals that the  $P_n$  will remain bounded only if  $A = 0$ .

The first and second moments are readily obtained upon differentiation of the normalized solution. The average radical populations derived in this manner are

$$\begin{aligned} \bar{n} &= aI_{(m+1)/2}(a/2)/4I_{(m-1)/2}(a/2) \\ \frac{\bar{n}}{n(n-1)} &= (a^2/16) - (m\bar{n}/2) \end{aligned} \quad (12)$$

The similarity to the expressions (6) is noteworthy. Only a reinterpretation of the kinetic parameters is required to obtain the proper value of  $\bar{n}$  from Figure 1.

Finally the case of negligible first-order processes is considered. The distribution then adopts the particularly simple form

$$P_n = (a/4)^n [e^{a/4} + (-1)^n e^{-a/4}] / 2n! \cosh (a/2) \quad (13)$$

with

$$\bar{n} = (a/4) \tanh (a/2) \\ \overline{n(n-1)} = a^2/16$$

As was anticipated, the polymerization rate, proportional to  $\bar{n}$ , lies between that predicted by Haward and the value for reaction in bulk. The average number of radical pairs associated with these models is independent of the extent of dispersed phase subdivision. The molecular weight, however, should decrease with increasing dispersion.

The selection of the appropriate model for a particular system is not always an obvious one. Examples for which radicals are produced in pairs within the hydrocarbon phase yet appear singly in the kinetic scheme are discussed by van der Hoff.<sup>5</sup> It seems plausible that such systems could be analyzed by means of a linear combination of the two models treated above. This can be accomplished simply by adding eqs. (1) and (8) weighted by the factors  $1 - b^2$  and  $b^2$ , respectively. The quantity  $b^2$  thus represents the fraction of free radicals which are initiated in pairs. The well behaved generating function can be obtained in terms of confluent hypergeometric functions as<sup>3</sup>

$$P = e^{ab(s-1)/4} \Phi(-c; m; - [(ab/2)(1+s)]) / \Phi(-c; m; - ab) \quad (14)$$

where

$$c = a(1 - b^2)/4b - (m/2)$$

Extraction of useful information from this solution would, in general, be a formidable task. There are however two interesting cases for which simplification prevails. First, it should be possible to arrive at the Haward model by setting  $m = 0$  and then allowing  $b^2$  to approach unity. Somewhat surprisingly this procedure predicts an average value for the radical population which is greater than that for reaction in bulk and in fact resembles the Smith-Ewart model more nearly than any pertaining to intraparticle initiation. It is

$$\bar{n} = (a/4) \coth (a/2) \quad (15)$$

Further inspection reveals that the physical picture, that of a complete absence of exchange of radicals with the continuous phase, simply does not define a mathematically unique system. Rather, the order in which the limits are taken is a determining factor.

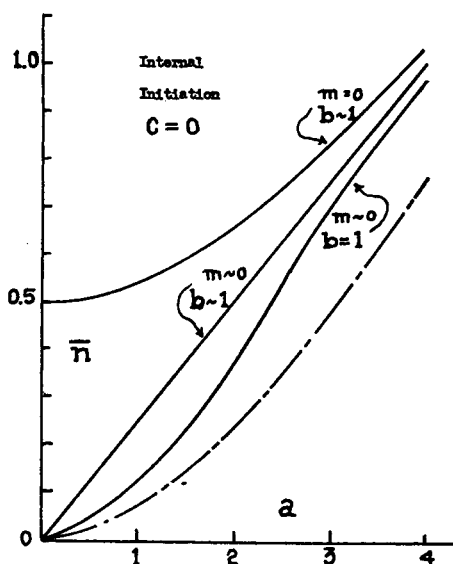


Fig. 3. Average radical population; (—) this work; (---) data of Haward.<sup>2</sup>

The second possibility for an explicit solution occurs when the parameter  $c$  takes on integral values and the  $\Phi$  becomes associated Laguerre polynomials  $L_c^{(m-1)}[(ab/2)(1+s)]$ . Of particular importance is the set of solutions for which  $c = 0$ . The radicals are then allotted according to the Poisson distribution:

$$P_n = e^{-\bar{n}}(\bar{n})^n/n! \quad (16)$$

with

$$\bar{n} = ab/4 = (1/4)(m^2 + a^2)^{1/2} - (m/4)$$

Reference to the kinetic significance of these parameters indicates that this case represents that of radical conservation in the continuous phase. The rate of molecular desorption is exactly balanced by that of re-entry. It would seem that this statement, together with the limit  $m \sim 0$ , best expresses in a definitive manner the model proposed by Haward. Application of this limit to the expression (16) yields a result which is indistinguishable from that for the corresponding homogeneous system:

$$\bar{n} = a/4$$

$$\overline{n(n-1)} = \bar{n}^2 \quad (17)$$

The rates of polymerization as predicted on the basis of the various interpretations of the intraparticle initiation model are presented in Figure 3.

In conclusion, two points should be emphasized: (1) dispersion of the reaction sites by means of emulsification can be expected to affect the macroscopic kinetics only if the continuous phase plays an active role;

(2) continued reduction of particle size will eventually have a deleterious effect on the conversion although augmented molecular weight may result.

### References

1. Stockmayer, W. H., *J. Polymer Sci.*, **24**, 314 (1957).
2. Haward, R. N., *J. Polymer Sci.*, **4**, 273 (1949).
3. Erdélyi, A., Ed., *Bateman Manuscript Project, Higher Transcendental Functions II*, McGraw-Hill, New York, 1953, pp. 79, 86, 189.
4. Smith, W. V., and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
5. van der Hoff, B. M. E., *Polymerization and Polycondensation Processes*, American Chemical Society Advances in Chemistry Series No. 34, Washington, 1962, p. 6.

### Résumé

La théorie quantitative des mécanismes par radicaux libres dans les polymérisations en émulsion a été réétudiée. On montre que les descriptions déjà existantes ne sont pas entièrement en accord avec les situations physiques réalisables. Les modifications proposées fournissent une ressemblance plus étroite avec les systèmes homogènes. On donne aussi des expressions explicites pour la distribution des radicaux. On met l'accent sur l'importance du transfert à l'interphase.

### Zusammenfassung

Die quantitative Theorie des radikalischen Mechanismus bei der Emulsionspolymerisation wird überprüft. Die bekannten Annahmen scheinen mit physikalisch realisierbaren Gegebenheiten nicht völlig vereinbar zu sein. Die vorgeschlagenen Änderungen führen zu einer engeren Verwandtschaft zu homogenen Systemen. Es werden explizite Ausdrücke für die Verteilung der Radikale angegeben. Die Wichtigkeit einer Interphasenübertragung wird betont.

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