# Theory of Compartmentalised Free-radical Polymerisation Reactions

By D. T. Birtwistle and D. C. Blackley[†]

(*Department of Mathematics and* [†]*National College of Rubber Technology, The Polytechnic of North London, Holloway,*
*London* N7 8DB)

*Summary* Explicit analytic solutions have been obtained for the variation with time of the various locus populations present in a compartmentalised free-radical polymerisation reaction in which the radicals are generated at a constant rate in a phase which is external and contiguous to the reaction loci, and in which the only significant processes which result in loss of radical activity from reaction loci are first order with respect to the concentration of radicals in the loci.

Explicit analytic solutions have been obtained for a problem to which Gilbert and Napper[1] have recently attempted to give approximate solutions by means of a matrix method. The problem is to calculate as a function of time $n_r$, the number of reaction loci containing $r$ radicals, for a seeded emulsion polymerisation which fulfils the following conditions: (i) radicals enter the reaction loci from an external phase at a constant rate, (ii) the only significant processes which result in loss of radical activity from reaction loci are kinetically of first order with respect to the concentration of radicals in the loci, (iii) radicals lost by diffusion from loci to the external phase are not available for re-initiation, (iv) the volume of the reaction loci is uniform and does not increase significantly as polymerisation proceeds, (v) no nucleation of new loci takes place, and (vi) no reduction in the total number of reaction loci occurs, *e.g.*, through agglomeration.

The general expression which we obtain for $n_r$ is given in equation (1), where $N$ is the total number of reaction loci,

$$n_r(t) = (N/r!)[\sigma(1-\mathrm{e}^{-kt})/k]^r \exp[-\sigma(1-\mathrm{e}^{-kt})/k] \tag{1}$$

$\sigma$ is the average rate of entry of radicals into a single locus, and $k$ characterises the rate of loss of radical activity by first-order processes. This result is obtained by re-casting the time-dependent Smith–Ewart recurrence relationships[2] for the assumed model in terms of a time-dependent generating function for numbers of loci. This generating function is defined as shown in equation (2), where $\xi$ is an

$$\Psi(\xi,t) = \sum_{i=0}^{\infty} n_i(t)\xi^i \tag{2}$$

auxiliary variable. This approach is in effect a generalisation of that used by Stockmayer[3] for the steady-state case. The expression obtained for the locus-number generating function is given in equation (3).

$$\Psi(\xi,t) = N\exp[\sigma(\xi - 1)(1 - \mathrm{e}^{-kt})/k] \tag{3}$$

Details of the derivation of these results for $\Psi(\xi,t)$ and $n_r(t)$ will be published in due course, together with a discussion of the implications of the result for $n_r(t)$ in respect of (i) the approach to the steady state, (ii) the average number of radicals per locus, and (iii) the rate of polymerisation. Attention is drawn here to the conclusion that the $n_r$ form a time-dependent Poisson distribution with respect to the $r$. The parameter of the distribution at any instant is, of course, the average number of radicals per locus at that instant.

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[3] W. H. Stockmayer, *J. Polymer Sci.*, 1957, **24**, 314.