Generalisation of a Theory of Compartmentalised Free-radical Polymerisation Reactions

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Summary The explicit analytic solutions reported previously for the variation with time of the various locus populations present in a compartmentalised free-radical polymerisation reaction have been generalised to cases where both the rate of radical influx and the parameter which characterises the loss of radicals are functions of time.

IN a recent note,[1] we have given an exact and explicit analytic solution to a problem to which Gilbert and Napper[2] had previously given an approximate solution obtained by means of a matrix method. The solution which we have reported has also been reported by Weiss and Dishon.[3] We have also given[4] the details of our derivation, together with a discussion of the implications of the result and of the type of reaction system to which it is expected to apply. One of the conclusions to which we have drawn attention is that the $n_r(t)$ form a time-dependent Poisson distribution with respect to the r, where $n_r(t)$ is the number of reaction loci which at time t contain exactly r propagating free radicals.

In the model formerly considered, radicals were assumed to enter the reaction loci at a constant rate, and the only significant processes which resulted in loss of radical activity from reaction loci were assumed to be kinetically of first order with respect to the concentration of radicals in the

loci. Loss by bimolecular termination was regarded as being of negligible importance. σ, the average rate of entry of radicals into a single locus, was taken to be constant over the period of the reaction, as also was the constant k which characterises the rate of loss of radical activity by first-order processes.

We have now found that it is possible to generalise our result to the case where both σ and k are functions of time. The generalised analysis still neglects radical-loss mechanisms which are other than first order in radical concentration. The characteristics of the generalised reaction system are governed by a function, $\theta(t)$, of time which can be obtained by solving the ordinary differential equation (1), and

$$d\theta(t)/dt = \sigma(t) - k(t)\cdot\theta(t) \tag{1}$$

inserting the initial condition $\theta(0) = 0$. [In this differential equation, σ and k are written as $\sigma(t)$ and $k(t)$ in order to emphasise their possible time-dependence.] Having obtained the function $\theta(t)$ for a particular case, it is then possible to write expressions for the locus-population generating function, $\Psi(\xi,t)$, the locus populations themselves, the average number of radicals per locus, $\bar{i}(t)$, and the total number of radicals in the reaction loci at time t, $\sum_{i=0}^{\infty} in_i(t)$. The results are given in equations (2)—(5), where

$$\Psi(\xi,t) = N\exp[(\xi - 1)\theta(t)] \tag{2}$$

$$n_r(t) = \{N[\theta(t)]^r/r!\}\exp[-\theta(t)] \tag{3}$$

$$\bar{i}(t) = \theta(t) \tag{4}$$

$$\sum_{i=0}^{\infty} in_i(t) = N\theta(t) \tag{5}$$

N is the total number of reaction loci in the system. It thus appears that the problem of predicting theoretically the characteristics of any particular reaction system of the class to which the theory applies can be reduced to that of solving a first-order ordinary differential equation involving t as the independent variable, rather than that of solving a first-order partial differential equation with ξ and t as independent variables.

Details of the derivation of the new results will be published in due course, together with the application of the method to a few cases of particular interest, notably, that where k is constant and σ is an exponentially decaying function of time. The significance of the theoretical predictions will be discussed. Attention is drawn here to the prediction that, whatever the nature of the time-dependence of σ and k, the n_r always form a time-dependent Poisson distribution with respect to the r. In fact, the function $\theta(t)$ is always the parameter of the distribution.

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[3] G. H. Weiss and M. Dishon, *J.C.S. Faraday I,* 1976, **72**, 1342.
[4] D. T. Birtwistle and D. C. Blackley, *J.C.S. Faraday I,* in the press.