Decay of Locus Populations in a Compartmentalised Free-radical Polymerisation Reaction upon Removal of Radical Source

By DAVID T. BIRTWISTLE, DAVID C. BLACKLEY,* and EAMON F. JEFFERS

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

Summary An explicit analytic solution has been obtained for the time-dependent Smith–Ewart equations for the case where the rate of formation of new radicals is zero, as would be the case if the rate of the radical-generating reaction in a compartmentalised free-radical polymerisation reaction were suddenly reduced to zero.

CONSIDERABLE effort has been devoted in recent years to the problem of finding analytic solutions to the Smith-Ewart equations[1] for compartmentalised free-radical polymerisation reactions. The equations have been shown to be completely soluble for the case of steady-state reactions,[2] but exact and explicit analytic solutions for non-steady-state reactions have so far been obtained only for those cases in which radicals are lost from reaction loci by processes which are first order in radical concentration in the locus.[3] In particular, these solutions do not apply to the important class of reactions in which the radical-loss mechanisms include bimolecular mutual termination within reaction loci. In developing solutions for this latter case, it has so far been necessary to resort to approximation procedures.[4]

We have recently found that it is possible to obtain an explicit analytic solution for the time-dependent Smith-Ewart equations for the general case of combined first- and second-order radical-loss reactions, provided that the rate of generation of new radicals within the reaction system is zero. The only restrictive assumption which it is necessary to make is the usual assumption that radicals which have been desorbed from the reaction loci are not subsequently available for re-initiation.

The type of reaction system to which our solution may be expected to apply could in principle be obtained as follows. (i) A compartmentalised free-radical polymerisation is first allowed to attain an equilibrium state, in which case the distribution of radicals within loci would be described by the Stockmayer–O'Toole solution[2] of the Smith–Ewart equations. (ii) The rate of generation of new radicals in the continuous phase of the reaction system is then suddenly reduced to zero, and the reaction is allowed to decay spontaneously. Possible ways in which the rate of generation of radicals might be reduced to zero include (a) release of a radical scavenger into the external phase, and (b) reducing the intensity of radiation to zero in the case of a radiation-initiated reaction.

$$\Psi(\xi,t) = N\sum_{p=0}^{\infty} B_p J_p^{(-1,m-1)}(\xi)\exp(-t/\tau_p) \tag{1}$$

We find that the locus-population generating function for this case can be expressed as an infinite series of Jacobi polynomials [equation (1)], where ξ is the auxiliary variable, t is time, m is the ratio kv/k_t, v being the volume of the individual reaction loci, and k and k_t being the rate coefficients for first-order radical loss processes and bimolecular termination respectively, $J_p^{(-1,m-1)}$ is a Jacobi-polynomial, the τ_p are characteristic relaxation times defined by equation (2), and N is the total number of reaction loci in the system. The coefficients B_p are given by

$$\tau_p = [(k_t/v)p(m + p - 1)]^{-1} \tag{2}$$

equation (3), where σ is the average rate of entry of radicals

$$B_p = \frac{2p + m - 1}{p+m-1} \times \frac{I_{m+2p-1}(\sqrt{8\sigma v/k_t})}{I_{m-1}(\sqrt{8\sigma v/k_t})} \tag{3}$$

into a single locus before the rate was reduced to zero, and I_ν is the modified Bessel function of the first kind of order ν. Equation (2) defines a spectrum of relaxation times, the totality of which, together with the associated intensities, characterises the decay of the reaction rate when the source of initiating radicals is removed.

Two quantities which are immediately derivable from the locus-population generating function given by equation (1) are (i) the numbers of loci, $n_r(t)$, which contain exactly r radicals at time t, and (ii) the average number of radicals per locus at time t, denoted by $\bar{i}(t)$. The results we obtain are given in equations (4) and (5).

$$n_r(t) = (N/2^r r!)\sum_{p=r}^{\infty} B_p(p+m-1)J_{p-r}^{(r-1,m+r-1)}(0) \times \exp(-t/\tau_p) \tag{4}$$

$$\bar{i}(t) = \tfrac{1}{2}\sum_{p=1}^{\infty}(m + p - 1)B_p \exp(t/\tau_p) \tag{5}$$

Full details of the derivation of these results will be given in due course, together with a discussion of their implications. In particular, it will be shown that, in principle, information concerning the quantities σ, k, and k_t can be obtained from measurements of rate of polymerisation as a function of time during the period which follows the cessation of the formation of new radicals in the external phase. We believe that this will provide a hitherto unexplored approach to the problem of obtaining experimental estimates of the quantities σ, k, and k_t. The full paper will include an application of the method to experimental results reported some years ago by Ley, Schneider, and Hummel.[5]

(*Received*, 27*th January* 1978; *Com.* 087.)

---

[1] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, 1948, **16**, 592.

[2] W. H. Stockmayer, *J. Polymer Sci.*, 1957, **24**, 314; J. T. O'Toole, *J. Appl. Polymer Sci.*, 1965, **9**, 1291.

[3] D. T. Birtwistle and D. C. Blackley, *J.C.S. Chem. Comm.*, 1977, 148, 783; *J.C.S. Faraday I*, 1977, **73**, 1998; G. H. Weiss and M. Dishon, *ibid.*, 1976, **72**, 1342.

[4] R. G. Gilbert and D. H. Napper, *J.C.S. Faraday I*, 1974, **70**, 391; B. S. Hawkett, D. H. Napper, and R. G. Gilbert, *ibid.*, 1977, **73**, 690.

[5] G. J. M. Ley, C. Schneider, and D. O. Hummel, *J. Polymer Sci., Part C*, 1969, **27**, 119.