Registry No. I (block copolymer), 107558-01-0; Ti(OBu)$_4$, 5593-70-4; alanine, 56-41-7.

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Emulsion Polymerizations. 3. Theory of Emulsion Copolymerization Kinetics[†]

Enzo Giannetti

Montefluos CRS, Montedison Group, Via S. Pietro 50, 20021 Bollate (Mi), Italy.

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ABSTRACT: On the basis of an extended Smith–Ewart theory, explicit analytic solutions are derived describing the locus population distribution of emulsion copolymerizing systems. By means of a two-variable transform, the infinite set of partial differential difference equations reduces to a single, highly symmetrical, linear partial differential equation whose solution gives the generating function for the $N_{r,i-r}$ number fraction of loci containing r growing radicals of type A and $i - r$ radicals of type B. Solutions to this equation, in both the stationary and nonstationary state, are given for the pseudohomopolymerization approach and for systems where termination by mutual annihilation is of negligible occurrence. On these grounds, it is concluded that, apart from very special cases, the pseudohomopolymerization approach represents a suitable approximation for systems of practical interest.

Introduction

Since its first appearance 40 years ago, the Smith–Ewart (SE) theory[1,2] has gained wide acceptance as providing a powerful tool to quantitatively describe free-radical compartmentalized polymerization of a wide range of monomers.[3,4] Based on appropriate extensions of this theory, a number of experimentally verified theoretical works now make possible a quantitative understanding and prediction of the dynamic and steady-state behavior of emulsion polymerizing systems. Examples include overall kinetics,[4,5] particle size distribution,[6] molecular weight distribution,[7,8] time evolution of the latex particle formation,[9-11] and so on. In view of the foregoing, apart from intrinsic interest, the extension of the SE theory to emulsion copolymerizing systems not only represents a natural complement but also may nourish advances similar to those made for emulsion homopolymerization. However, this step is not trivial at all. The large number of rate coefficients involved in this process represents a formidable task to the development of a simple mathematical approach to a quantitative description of the overall kinetics of these systems.

A previous paper in this series[12] derived the two-dimensional molecular weight distribution function of emulsion copolymers from a simple probabilistic approach. The distribution of locus population $N_{r,i-r}(t)$, i.e., the number density of reaction loci per unit volume containing r radicals of type A and $i - r$ radicals of type B, has been described through the pseudohomopolymerization approach proposed some years ago by Ballard et al. and Nomura and co-workers.[13] Although this approach seems to represent a quite reasonable approximation for many systems of practical interest, there is still a paucity of knowledge in the space parameter region where this approximation holds true. Accordingly, this paper addresses a solution to the complete SE population balance equations for emulsion copolymers.

For a better understanding of the concepts developed hereafter, it is worthwhile to briefly introduce some fundamental principles of the emulsion copolymerization process. Basically, the time evolution of the locus population distribution is given in terms of simple population balance equations leading to an extended SE theory for copolymers.[13] In the following section the pseudohomopolymerization approach[12,13] will be derived rigorously by introducing an appropriate locus population generating function. Subsequently, it will be shown how the infinite set of differential difference extended SE equations for emulsion copolymers can be reduced to a single, highly symmetrical partial differential equation by applying a suitable two-variable transform. Finally, explicit analytic solutions will be given for the $N_{r,i-r}$ distribution, in both the steady and nonsteady state, for a seeded emulsion copolymerization where the only significant processes that

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[†] For part 2, see ref 12.

result in loss of radical activity from reaction loci are kinetically first order with respect to the concentration of radicals.

Background

A monodispersed latex system is considered where no new reaction loci are formed and where particle volume does not vary with time. Moreover, the monomer concentrations within the latex particles are taken to be constant throughout the reaction. The main locus of polymerization is inside the latex particles; i.e., we neglect polymer growth in the water phase. In the system two different monomer units, A and B, can react together through a free-radical mechanism to form linear copolymer chains of varying lengths. Different kinds of elementary events relevant to the $N_{r,i-r}(t)$ locus population distribution need to be taken into account.[13]

Radicals are presumed to be generated in the external phase at a constant rate. This process is assumed to be kinetically zero order with respect to the concentration of the active radicals within the latex particles. Once a radical enters a reaction locus it is presumed to initiate a chain growth reaction which continues at a constant rate until the activity of the radical is lost. In turn, the processes whereby the activity of the radical is lost fall into two broad categories: (i) processes that are kinetically first order with respect to the concentration of growing radicals, e.g., exit of the radical into the external phase and/or spontaneous deactivation and (ii) processes that are kinetically second order with respect to the concentration of radicals in the reaction locus. Bimolecular termination by mutual annihilation is by far the most important.

These three classes of elementary events account for the $N_i(t)$ distribution, i.e., the relative number of latex particles containing i free radicals at reaction time t. However, the complete description of emulsion copolymerizing systems requires the knowledge not only of the $N_i(t)$ distribution but also of the $N_{r,i-r}(t)$ locus population distribution function, i.e., the relative number of latex particles containing i free radicals at time t, r of which are of type A and $i - r$ of which are of type B. In the following treatment it is worthwhile choosing these distributions to be normalized so that

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}N_{r,i-r}(t) = \sum_{i=0}^{\infty}N_i(t) = 1 \qquad (1)$$

The average number of radicals per latex particle $\bar{n}_{\mathrm{tot}}$ is given simply by the first moment of the $N_i(t)$ distribution.

$$\bar{n}_{\mathrm{tot}} = \sum_{i=1}^{\infty}iN_i(t) \qquad (2)$$

Furthermore also $\bar{n}_{\mathrm{A}}$ and $\bar{n}_{\mathrm{B}}$, the average number of A radicals and B radicals per particle, are related in a simple fashion to the $N_{r,i-r}(t)$ distribution function and to $\bar{n}_{\mathrm{tot}}$.

$$\bar{n}_{\mathrm{A}} = \sum_{i=1}^{\infty}\sum_{r=0}^{i}rN_{r,i-r} \qquad (3a)$$

$$\bar{n}_{\mathrm{B}} = \sum_{i=1}^{\infty}\sum_{r=0}^{i}(i-r)N_{r,i-r}(t) \qquad (3b)$$

$$\bar{n}_{\mathrm{tot}} = \bar{n}_{\mathrm{A}} + \bar{n}_{\mathrm{B}} \qquad (3c)$$

To account for the $N_{r,i-r}(t)$ time evolution all the rate coefficients for population gain and loss must be specified for the kinetic order with respect to both the concentration and the nature of the radicals involved. Thus, we must consider ρ_{A} and ρ_{B}, the rate coefficients for entry of radicals A and B, respectively, and k_{A} and k_{B}, the rate coefficients for exit of radical species A and B. Concerning bimolecular termination events, for a first-order Markov process, the binary radical copolymerization of monomer A and B can be completely specified by three termination rate constants: c_{AA}, c_{BB}, and c_{AB} (note that $c_{\mathrm{AB}} = c_{\mathrm{BA}}$). All the aforementioned elementary reactions cause the overall number of growing radicals to vary. However, when dealing with emulsion copolymerizing systems, one has to account for a further class of elementary events: those by which the overall number i of growing radicals is left unchanged whereas the relative numbers of radicals of type A and radicals of type B are varied. This kind of process is first order with respect to the concentration of radicals (of type A and/or type B). They are accounted for by the cross-transfer and cross-propagation rate constants γ_{A} and γ_{B} defined as

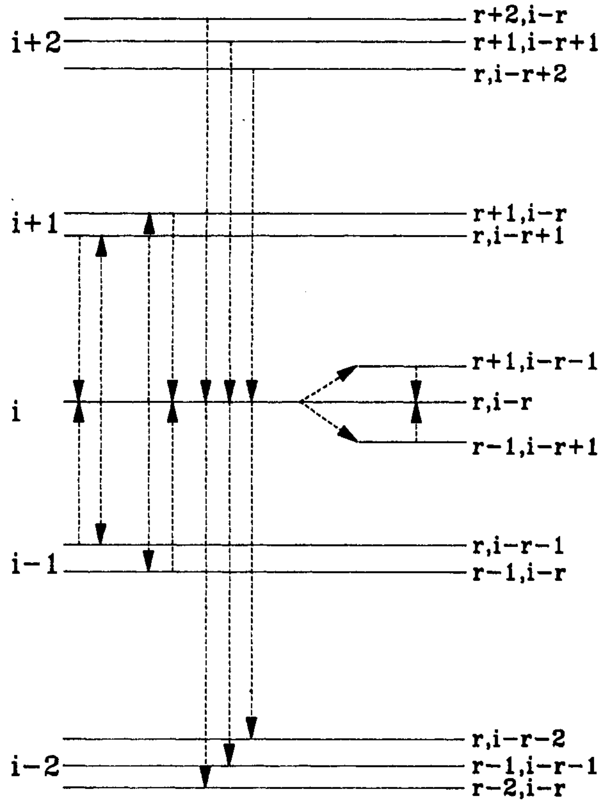

Figure 1. Transitions between states of radical occupancy required for the derivation of the time-dependent Smith–Ewart differential difference equation for state r, $i - r$. The levels of higher radical occupancy are displayed above states of lower occupancy.

$$\gamma_{\mathrm{A}} = (k_{\mathrm{p,AB}} + k_{\mathrm{tr,AB}})C_{\mathrm{MB}} \qquad (4a)$$

$$\gamma_{\mathrm{B}} = (k_{\mathrm{p,BA}} + k_{\mathrm{tr,BA}})C_{\mathrm{MA}} \qquad (4b)$$

where C_{MA} and C_{MB} denote the concentrations within the latex particles of monomer A and monomer B, respectively.

The fundamental equations that govern the behavior of a compartmentalized free-radical copolymerization reaction are more easily grasped by considering the rates of the various processes by which loci containing exactly i propagating radicals, r of which of type A and $i - r$ of type B, are formed and destroyed. The processes are illustrated in Figure 1 as transitions between mutually connected states of the reacting system, each state being defined as the number of propagating radicals of type A and B present in the locus. There are four processes by which loci containing r growing radicals of type A and $i - r$ of type B can be formed: (i) by acquisition of a radical of type A or B from type $i - 1$ loci; (ii) by loss of a radical of type A or B from type $i + 1$ loci; (iii) from $i + 2$ loci by mutual termination within these loci; (iv) by cross-reactions from connected loci containing the same number i of overall radicals.

Likewise, there are four processes by which loci of type $N_{r,i-r}(t)$ can be destroyed: (i) by acquisition of a further radical (of type A or B); (ii) by loss of a radical (A or B) by first-order processes (exit or monomolecular termination); (iii) by loss of two radicals by mutual annihilation; (iv) by loss of a radical by cross-reactions.

The difference between the sum of the rates of the first group of processes and the sum of the rates of the second one gives the time evolution of the $N_{r,i-r}(t)$ distribution.[13]

$$\begin{aligned}\frac{\mathrm{d}N_{r,i-r}}{\mathrm{d}t} = {} & -[\rho_A + \rho_B + rk_A + (i-r)k_B + r(r-1)c_{AA} + \\ & 2r(i-r)c_{AB} + (i-r)(i-r-1)c_{BB} + r\gamma_A + \\ & (i-r)\gamma_B]N_{r,i-r} + \rho_A N_{r-1,i-r} + \\ & \rho_B N_{r,i-r-1} + (r+1)k_A N_{r+1,i-r} + (i-r+1)k_B N_{r,i-r+1} + \\ & (r+2)(r+1)c_{AA}N_{r+2,i-r} + \\ & 2(r+1)(i-r+1)c_{AB}N_{r+1,i-r+1} + \\ & (i-r+2)(i-r+1)c_{BB}N_{r,i-r+2} + (r+1)\gamma_A N_{r+1,i-r-1} + \\ & (i-r+1)\gamma_B N_{r-1,i-r+1} \qquad (5)\end{aligned}$$

Equation 5 comprises an infinite set of linear differential difference equations. They constitute an extended SE mechanism for emulsion copolymerization. To the extent that relative numbers of loci and numbers of radicals are regarded as mere numbers and therefore dimensionless, both the left- and right-hand side dimensions of eq 5 become [time]$^{-1}$. Accordingly the dimension of the rate constants ρ_i, k_i, γ_i, and c_{ij} (i, j = A, B) is also [time]$^{-1}$. Consequently, in the following treatment, rate constants should be regarded as pseudo-first-order rate parameters rather than true rate constants. No attempt is made to determine an a priori dependence on polymerization conditions such as the overall number of latex particles per unit volume N_c, particle size distribution, ionic strength, surfactant concentration, polymer weight fraction, and so on.

The Pseudohomopolymerization Approach

As already pointed out in a previous work,[12] two distinctive kinds of elementary processes can be identified in the time-dependent $N_{r,i-r}(t)$ population balance eq 5: those affecting the overall number i of growing radicals (vertical transitions) and those affecting only their nature (horizontal transitions). These two classes of processes occur under considerably different time scales. Actually, most copolymers of practical interest have a degree of polymerization at least of 10^3 or even higher. In contrast, the mean length of sequences of equal monomer units is more than 1 order of magnitude lower. As a consequence, one can safely assume that any growing radical undergoes many more transitions between states having the same number of radicals i than between states labeled by different i. Accordingly, for binary statistical copolymers, apart from special circumstances, vertical and horizontal transitions are very weakly coupled. This enables one to obtain from eq 5 the following set of reduced population balance equations simply by neglecting all terms but those containing the rate coefficients γ_A and γ_B:

$$\begin{aligned}\frac{\mathrm{d}N_{r,i-r}}{\mathrm{d}t} = {} & -[r\gamma_A + (i-r)\gamma_B]N_{r,i-r} + \\ & (r+1)\gamma_A N_{r+1,i-(r+1)} + [i-(r-1)]\gamma_B N_{r-1,i-(r-1)} \qquad (6)\end{aligned}$$

Equation 6 constitutes a *finite* set of differential difference equations. Like Stockmayer[14] and Blackley,[15] we seek a solution in terms of a simple locus population generating function. In this method the set of linear differential equations (6) is converted into a single equation. A new function $\Psi_i(\xi,t)$ is introduced, defined by the equation

$$\Psi_i(\xi,t) = \sum_{r=0}^{i} N_{r,i-r}(t)\xi^r \qquad (7)$$

where ξ is an auxiliary variable and the subscript i means that the generating function refers to latex particles containing an overall number i of growing radicals. Furthermore, for the sake of simplicity, the latex particle distribution $N_{r,i-r}(t)$ is normalized such that

$$\Psi_i(1,t) = \sum_{r=0}^{i} N_{r,i-r}(t) = N_i(t) = 1 \qquad (8)$$

All the fractional locus population $N_{r,i-r}(t)$ at all time can, in principle, be obtained from the function $\Psi_i(\xi,t)$ making use of the fact that[5]

$$N_{r,i-r}(t) = \frac{1}{r!}\left(\frac{\partial^r \Psi_i}{\partial \xi^r}\right)_{\xi=0} \qquad (9)$$

In order to convert the set of differential difference equations (6) into a single differential equation having Ψ_i as the independent variable, each equation for $\mathrm{d}N_{r,i-r}/\mathrm{d}t$ is multiplied by ξ^r and then all equations so obtained are added together. It is noted that

$$\sum_{r=0}^{i} rN_{r,i-r}\xi^r = \xi\,\partial\Psi_i/\partial\xi; \qquad \sum_{r=0}^{i} N_{r-1,i-(r-1)}\xi^r = \xi\Psi_i;$$
$$\sum_{r=0}^{i}(r+1)N_{r+1,i-(r+1)}\xi^r = \partial\Psi_i/\partial\xi;$$
$$\sum_{r=0}^{i}(r-1)N_{r-1,i-(r-1)}\xi^r = \xi^2\partial\Psi_i/\partial\xi \qquad (10)$$

where in each case the summation covers all possible values of r. The resulting single differential equation then readily transforms to

$$\partial\Psi_i/\partial t = (1-\xi)[(\xi\gamma_B + \gamma_A)\partial\Psi_i/\partial\xi - i\gamma_B\Psi_i] \qquad (11)$$

The solution to eq 11 has to be subjected to the initial boundary conditions, which for the case under examination (i.e., ab initio seeded emulsion copolymerization), are the following

$$\Psi_i(\xi,0) = 1 \quad (i > 0); \qquad \Psi_i(1,t) = 1 \qquad (12)$$

For the special case of systems which are in steady state $\partial\Psi_i/\partial t = 0$ so that in the right-hand side of eq 11 the partial differential coefficient of $\Psi_i(\xi,t)$ with respect to ξ becomes the ordinary differential coefficient. Moreover, dividing through by the factor $(1-\xi)$ then gives

$$(\gamma_B\xi + \gamma_A)\,\mathrm{d}\Psi_i/\mathrm{d}\xi - i\gamma_B\Psi_i = 0 \qquad (13)$$

The following steady-state solution results:

$$\Psi_i = \left(\frac{\xi + h}{1 + h}\right)^i; \qquad h = \gamma_A/\gamma_B \qquad (14)$$

From eq 14 it immediately follows that

$$N_{r,i-r} = \binom{i}{r}\frac{\gamma_A{}^{i-r}\gamma_B{}^r}{(\gamma_A + \gamma_B)^i} = P_{r,i-r} \qquad (15)$$

where $P_{r,i-r}$ represents the number fraction of latex particles in state i containing r growing radicals of type A and $i-r$ of type B. By substituting eq 15 into eq 5 and summing up from $r = 0$ to $r = i$, the classical SE equations for homopolymerization can be derived, provided that the following pseudohomopolymerization rate constants are introduced:

$$\bar{\rho} = \rho_A + \rho_B \quad (16a)$$

$$\bar{k} = \frac{k_A\gamma_B + k_B\gamma_A}{(\gamma_A + \gamma_B)} \quad (16b)$$

$$\bar{c} = \frac{\gamma_B^2 c_{AA} + 2\gamma_A\gamma_B c_{AB} + \gamma_A^2 c_{BB}}{(\gamma_A + \gamma_B)^2} \quad (16c)$$

No analytic solution to eq 11 is available in the non steady state. Actually although the Fourier method of variables separation can still be applied, the function $\Psi_i(\xi,t)$ becomes infinite at the normalization point $\xi = 1$. This result is not physically acceptable since the necessary constraint $\Psi_i(1,t) = 1$ cannot be fulfilled at all. It can be easily recognized that the assumption of horizontal transitions independent of vertical ones no longer holds true when dealing with non-steady-state SE equations. Our reasoning is the following. For an ab initio seeded emulsion copolymerizing system the only mechanism whereby state i becomes populated is acquisition of a radical from type $i - 1$ loci. In turn this means that adjacent states of the system should be connected to each other by some elementary process (radical entry in the present case).

This notwithstanding, it is possible to gain useful information about the rate parameters governing characteristic relaxation time of horizontal versus vertical transitions. To this end we consider a set of equations which, under certain circumstances, can be regarded as being a reasonable approximation of eq 6. In this connection the following partial differential equation has to be taken into account:

$$\partial\Psi_i/\partial t = (1 - \xi)[(\gamma_A + \gamma_B)\partial\Psi_i/\partial\xi - i\gamma_B\Psi_i] \quad (17)$$

Practically, in the term multiplying $\partial\Psi_i/\partial\xi$ on the right-hand side of eq 11, the factor ξ has been replaced by 1. The consequence of the proposed approximation is consistent with the following set of SE differential difference equations:

$$\begin{aligned} \mathrm{d}N_{r,i-r}/\mathrm{d}t = -\{r\gamma_A N_{r,i-r} + \gamma_B[iN_{r,i-r} + \\ (r + 1)N_{r+1,i-(r+1)}]\} + (r + 1)\gamma_A N_{r+1,i-(r+1)} + \\ \gamma_B[iN_{r-1,i-(r-1)} - rN_{r+1,i-(r+1)}] \quad (18) \end{aligned}$$

Comparison between eq 5 and eq 18 shows that in the latter the factor $rN_{r,i-r}$ has been replaced by the factor $(r + 1)N_{r+1,i-(r+1)}$ and $(r - 1)N_{r-1,i-(r-1)}$ by $rN_{r,i-r}$. These replacements seem justified provided $N_{r+1,i-(r+1)} \sim N_{r,i-r} \sim N_{r-1,i-(r-1)}$. This condition is fulfilled whenever $i \gg 1$ and $r \simeq i/2$. Equation 17 is satisfied by the function

$$\Psi_i(\xi,t) = \exp[(\xi - 1)\vartheta(t)] \quad (19)$$

if $\vartheta(t)$ is a function of time which satisfies the ordinary differential equation

$$\mathrm{d}\vartheta/\mathrm{d}t = i\gamma_B - [\gamma_A + \gamma_B]\vartheta \quad (20)$$

For the system under consideration, the boundary condition indicates that $\Psi_i(\xi,0) = 1$, i.e., $\vartheta(0) = 0$. Accordingly, eq 20 allows the following equation to be written:

$$\vartheta(t) = ih/(1 + h)\{1 - \exp[-(\gamma_A + \gamma_B)t]\} \quad (21)$$

Equation 19 is immediately recognizable as the frequency generating function for a Poisson distribution whose parameter is $\vartheta(t)$. Accordingly, we obtain

$$P_{r,i-r}(t) = \frac{[\vartheta(t)]^r}{r!}\exp[-\vartheta(t)] \quad (22)$$

In the steady state $\vartheta(\infty) = ih/(1 + h)$. As is well-known the resulting Poisson distribution converges to eq 15 when r is large.[16] The overall $N_{r,i-r}(t)$ distribution may be expressed accordingly

$$N_{r,i-r}(t) = N_i(t)P_{r,i-r}(t) \quad (23)$$

As shown by Blackely and Birtwistle,[5] a satisfactory approximation to the non-steady-state $N_i(t)$ distribution is given by a simple Poisson distribution, provided bimolecular termination is not the main chain-stopping event.

$$N_i(t) = \frac{[\varphi(t)]^r}{r!}\exp[-\varphi(t)] \quad (24)$$

The time-dependent parameter $\varphi(t)$ is a function of the Stockmayer–O'Toole m and α kinetic rate parameters. Basically, under the above-mentioned approximations, we can conclude that horizontal transitions occur on time scales determined mainly by $(\gamma_A + \gamma_B)$, whereas characteristic time for vertical transitions depends on the Stockmayer–O'Toole m and α parameters. For most systems of practical interest, these two sets of kinetic constants differ by more than 1 order of magnitude. However, for emulsion block copolymers and when dealing with the non-stationary state, this approximation holds true no longer so that the complete population balance eq 5 need to be taken into account.

Solution to the Complete SE Equations

When dealing with a time-dependent infinite set of partial differential difference equations, the mathematical handling of the system can be greatly simplified by applying suitable transforms. Very often a simple power transform allows a single partial differential equation to be written. In the present case, one has to account at the same time for two different distributions, one of radicals of type A and one of radicals of type B. Consequently, a two auxiliary variable transform has to be applied. This approach has been successfully employed some years ago by Ray et al.[17] for a comprehensive treatment of the two-dimensional MWD distribution functions of binary statistical copolymers.

The infinite set of population balance equations (5) can be converted into a single equation by using different kinds of two-variable power transforms. However, particular attention has to be drawn to the symmetry of the problem. For this reaction, it is worthwhile to seek a generating function

$$\Psi(\xi,\lambda,t) = \sum_{i=0}^{\infty}\sum_{r=0}^{i}\xi^i\lambda^{-r}N_{r,i-r}(t) \quad (25)$$

which is such that, when expanded as a power series in the auxiliary variables ξ and λ the coefficient of $\xi^i\lambda^{-r}$ is $N_{r,i-r}(t)$. Such a generating function arises from the combination of two types of transforms: a simple power transform and an inverse power transform (ζ transform). It is convenient to choose the new λ variable such that $\lambda = \xi/\zeta$. The resulting generating function is

$$\Psi(\zeta,\xi,t) = \sum_{i=0}^{\infty}\sum_{r=0}^{i}N_{r,i-r}(t)\zeta^r\xi^{i-r} \quad (26)$$

Once the $\Psi(\zeta,\xi,t)$ function is known, all the fractional locus populations at all times can be derived from it, making use of the fact that

$$N_{r,i-r}{}^{(t)} = \frac{1}{i!}\binom{i}{r}\left[\frac{\partial^r}{\partial\zeta^r}\left(\frac{\partial^{i-r}\Psi}{\partial\xi^{i-r}}\right)\right]_{\zeta,\xi=0} \quad (27)$$

Furthermore, the average number of propagating radicals

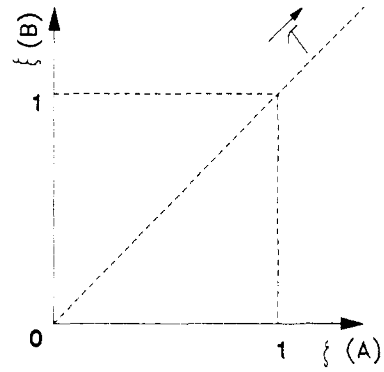

Figure 2. Region of the ζ,ξ plane where the generating function Ψ is defined.

of type A, $\bar{n}_A(t)$, and type B, $\bar{n}_B(t)$, can be found from the following relationships:

$$\bar{n}_A(t) = (\partial\Psi/\partial\zeta)_{\zeta,\xi=1} \tag{28a}$$

$$\bar{n}_B(t) = (\partial\Psi/\partial\xi)_{\zeta,\xi=1} \tag{28b}$$

This means that by using the generating function Ψ the two auxiliary variables ζ and ξ *behave independently*: ζ accounts for radicals for type A and ξ for radicals of type B. This is not the case for different combinations of transforms such as

$$\Psi^*(\zeta,\xi,t) = \sum_{i=0}^{\infty} \sum_{r=0}^{i} N_{r,i-r}(t)\zeta^i\xi^r$$

where the variables account at the same time for radicals of type A and B. Moreover, the generating function Ψ has the following additional properties:

(i) $$\Psi(1,1,t) = \sum_{i=0}^{\infty} \sum_{r=0}^{i} N_{r,i-r}(t) = 1 \qquad \text{for all } t \tag{29}$$

(ii) The relative number density of radical pairs of type A–A, B–B, and A–B is given by

$$\sum(\text{A–A})\text{pairs} = \tfrac{1}{2}(\partial^2\Psi/\partial\zeta^2)_{\zeta=\xi=1} \tag{30a}$$

$$\sum(\text{B–B})\text{pairs} = \tfrac{1}{2}(\partial^2\Psi/\partial\xi^2)_{\zeta=\xi=1} \tag{30b}$$

$$\sum(\text{A–B})\text{pairs} = \partial/\partial\xi(\partial\Psi/\partial\zeta)_{\zeta=\xi=1} \tag{30c}$$

(iii) Along the line parametrically defined by $\vec{\tau} = 2^{1/2}/2\zeta$ and $\vec{\tau} = 2^{1/2}/2\xi$ (see Figure 2), the generating function Ψ reduces to the corresponding SE generating function for homopolymerization.

To be acceptable, the generating function must be such that both $(\partial^r\Psi/\partial\zeta^r)_{\zeta=\xi=1}$ and $(\partial^r\Psi/\partial\xi^r)_{\zeta=\xi=1}$ are finite for all r. This follows because physically these quantities represent the sums of products of number densities of loci and numbers of radicals.

To convert the set of differential difference equations (5) into a single equation in Ψ, each equation for $dN_{r,i-r}/dt$ is multiplied by $\zeta^r\xi^{i-r}$, and then all the equations so obtained are summed over r and over i, where it is understood that $N_{-1,0} = N_{0,-1} = 0$. By making use of the relationships in Table I, eq 5 transforms to

$$\frac{\partial\Psi}{\partial t} = -[\rho_A(1-\zeta) + \rho_B(1-\xi)]\Psi + [k_A(1-\zeta) + \gamma_A(\xi-\zeta)]\frac{\partial\Psi}{\partial\zeta} + [k_B(1-\xi) + \gamma_B(\zeta-\xi)]\frac{\partial\Psi}{\partial\xi} + c_{AA}(1-\zeta^2)\frac{\partial^2\Psi}{\partial\zeta^2} + 2c_{AB}(1-\zeta\xi)\frac{\partial^2\Psi}{\partial\zeta\partial\xi} + c_{BB}(1-\xi^2)\frac{\partial^2\Psi}{\partial\xi^2} \tag{31}$$

Table I
Relationships between the Locus Population Summations and the Generating Function $\Psi(\zeta,\xi,t)$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i} N_{r,i-r}\zeta^r\xi^{i-r} = \Psi; \qquad \sum_{i=0}^{\infty}\sum_{r=0}^{i} N_{r-i,i-r}\,\zeta^r\xi^{i-r} = \zeta\Psi$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i} rN_{r,i-r}\zeta^r\xi^{i-r} = \zeta\frac{\partial\Psi}{\partial\zeta}; \qquad \sum_{i=0}^{\infty}\sum_{r=0}^{i}(i-r)N_{r,i-r}\zeta^r\xi^{i-r} = \xi\frac{\partial\Psi}{\partial\xi}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}N_{r,i-r-1}\zeta^r\xi^{i-r} = \xi\Psi; \qquad \sum_{i=0}^{\infty}\sum_{r=0}^{i}(r+1)N_{r+1,i-r}\zeta^r\xi^{i-r} = \frac{\partial\Psi}{\partial\zeta}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(i-r+1)N_{r,i-r+1}\zeta^r\xi^{i-r} = \frac{\partial\Psi}{\partial\xi};$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(r+1)N_{r+1,i-(r+1)}\zeta^r\xi^{i-r} = \xi\frac{\partial\Psi}{\partial\zeta}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(i-r+1)N_{r-1,i-r+1}\zeta^r\xi^{i-r} = \zeta\frac{\partial\Psi}{\partial\xi};$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}r(r-1)N_{r,i-r}\zeta^r\xi^{i-r} = \zeta^2\frac{\partial^2\Psi}{\partial\zeta^2}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}r(i-r)N_{r,i-r}\zeta^r\xi^{i-r} = \zeta\xi\frac{\partial}{\partial\zeta}\,\frac{\partial\Psi}{\partial\xi};$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(i-r)(i-r-1)N_{r,i-r}\zeta^r\xi^{i-r} = \xi^2\frac{\partial^2\Psi}{\partial\xi^2}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(r+2)(r+1)N_{r+2,i-r}\zeta^r\xi^{i-r} = \frac{\partial^2\Psi}{\partial\zeta^2}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(r+1)(i-r+1)N_{r+1,i-(r+1)}\zeta^r\xi^{i-r} = \frac{\partial}{\partial\xi}\,\frac{\partial\Psi}{\partial\zeta} = \frac{\partial}{\partial\zeta}\,\frac{\partial\Psi}{\partial\xi}$$

$$\sum_{i=0}^{\infty}\sum_{r=0}^{i}(i-r+2)(i-r+1)N_{r,i-r+2}\,\zeta^r\xi^{i-r} = \frac{\partial^2\Psi}{\partial\xi^2}$$

This highly symmetrical partial differential "wave equation" has to be solved satisfying the initial boundary conditions appropriate for the particular case under examination.

For the special case of systems that are in steady state, $\partial\Psi/\partial t = 0$ and the right-hand side of eq 31 must be zero. As a consequence, contrary to emulsion homopolymerizations, the solution of the stationary-state wave equation for emulsion copolymerizations still involves partial differential equations of the type

$$[\rho_A(1-\zeta) + \rho_B(1-\xi)]\Psi = [k_A(1-\zeta) + \gamma_A(\xi-\zeta)]\frac{\partial\Psi}{\partial\zeta} + [k_B(1-\xi) - \gamma_B(\zeta-\xi)]\frac{\partial\Psi}{\partial\xi} + c_{AA}(1-\zeta^2)\frac{\partial^2\Psi}{\partial\zeta^2} + 2c_{AB}(1-\zeta\xi)\frac{\partial^2\Psi}{\partial\zeta\partial\xi} + c_{BB}(1-\xi^2)\frac{\partial^2\Psi}{\partial\xi^2} \tag{32}$$

Results and Discussion

For the particular case in which the radical loss reactions of second order are of negligible occurrence with respect to those of the first order, i.e., when $c_{AA} = c_{BB} = c_{AB} = 0$, eq 32 reduces to

$$[\rho_A(1-\zeta) + \rho_B(1-\xi)]\Psi = [k_A(1-\zeta) + \gamma_A(\xi-\zeta)]\partial\Psi/\partial\zeta + [k_B(1-\xi) + \gamma_B(\zeta-\xi)]\partial\Psi/\partial\xi \tag{33}$$

In order to apply the method of variable separation to eq 33, it is necessary to transform the (ζ,ξ) plane into a new (u,v) plane according to the following linear equations

$$\zeta = au + v \tag{34a}$$

$$\xi = u - bv \tag{34b}$$

where a and b are two constants. The related Jacobian of this plane transformation is

$$\mathbf{J} = \frac{1}{1+ab}\begin{vmatrix} b & 1 \\ 1 & -a \end{vmatrix} \tag{35}$$

so that the following expressions result for the new variables

$$u = 1/C(b\zeta + \xi) \tag{36a}$$

$$v = 1/C(\zeta - a\xi) \tag{36b}$$

$$C = (1 + ab) \tag{36c}$$

Since the transform must map the $\Psi(\zeta,\xi)$ function onto a new $\Phi(u,v)$ function for every (ζ,ξ) in the plane region $\|\mathbf{R}\| \equiv 0 \leqslant (\zeta,\xi) \leqslant 1$ and vice versa, it follows that the condition $|\mathbf{J}| \neq 0$ must be fulfilled everywhere in $\|\mathbf{R}\|$, and consequently, it must be $ab \neq -1$. Equation 33 transforms into a new linear partial differential equation where the coefficients with respect to the partial derivatives are each functions only of their own variable if the a and b parameters of the linear transform satisfy the following equations

$$\gamma_A b^2 + (\sigma_A - \sigma_B)b - \gamma_B = 0 \tag{37a}$$

$$\gamma_B a^2 + (\sigma_A - \sigma_B)a - \gamma_A = 0 \tag{37b}$$

where

$$\sigma_i = k_i + \gamma_i; \qquad i = A, B \tag{37c}$$

Accordingly, by imposing

$$a = \frac{-(\sigma_A - \sigma_B) - [(\sigma_A - \sigma_B)^2 + 4\gamma_A\gamma_B]^{1/2}}{2\gamma_B} \tag{38a}$$

$$b = a\gamma_B/\gamma_A \tag{38b}$$

the following partial differential equation results

$$[\rho_t - (\rho_u u + \rho_v v)]\Phi = 1/C\{(k_u - \gamma_u u)\partial\Phi/\partial u + (k_v - \gamma_v v)\partial\Phi/\partial v\} \tag{39}$$

where

$$\rho_t = \rho_A + \rho_B; \qquad \rho_u = a\rho_A + \rho_B; \qquad \rho_v = \rho_A - b\rho_B \tag{39a}$$

$$k_u = bk_A + k_B; \qquad k_v = k_A - ak_B \tag{39b}$$

$$\gamma_u = (ab\sigma_A + \sigma_B) - (b\gamma_A + a\gamma_B); \qquad \gamma_v = (\sigma_A + ab\sigma_B) + (b\gamma_A + a\gamma_B) \tag{39c}$$

If the function $\Phi(u,v)$ is assumed to be of the form $\varphi(u)\vartheta(v)$ the problem becomes one of solving the two ordinary differential equations

$$(\rho_t - \rho_u u) - 1/C(k_u - \gamma_u u)\ \mathrm{d}\ \ln \varphi(u) = \lambda \tag{40a}$$

$$1/C(k_v - \gamma_v)\ \mathrm{d}\ \ln \vartheta(v) + \rho_v v = \lambda \tag{40b}$$

where λ is a separation constant. The solution to eq 40a is

$$\varphi(u) = A(k_u - \gamma_u u)^{\beta} \exp\{-C[\rho_u/\gamma_u{}^2(k_u - \gamma_u u)]\} \tag{41}$$

where A is a constant whose value may depend upon that of λ. The solution to eq 40b is

$$\vartheta(v) = B(k_v - \gamma_v v)^{\eta} \exp\{-C[\rho_v/\gamma^2(k_v - \gamma_v v)]\} \tag{42}$$

where B is a second constant whose value may also depend upon that of λ. In turn, both β and η are related to the separation constant through the following relationships

$$\beta = C/\gamma_u[(\rho_u k_u)/\gamma_u - \rho_t + \lambda] \tag{43a}$$

$$\eta = C/\gamma_v[(\rho_v k_v)/\gamma_v - \lambda] \tag{43b}$$

These two exponentials are not independent from each other, being related according to the equation

$$\beta = C/\gamma_u[(\rho_u k_u)/\gamma_u + (\rho_v k_v)/\gamma_v - \rho_t - \eta\gamma_v/C] \tag{44}$$

However, after some cumbersome algebra, it is possible to demonstrate that

$$\rho_t - \left(\frac{\rho_u k_u}{\gamma_u} + \frac{\rho_v k_v}{\gamma_v}\right) = 0 \tag{45}$$

so that eq 44 reduces itself to

$$\beta = -\eta(\gamma_v/\gamma_u) \tag{46}$$

A particular solution to eq 39, for a particular value of λ, is the function

$$\Phi(u,v,\lambda) = C(\lambda)\varphi(u)\vartheta(v) \tag{47}$$

where C is a composite constant whose possible dependence upon λ is emphasized by writing it as $C(\lambda)$. According to the superposition principle in the theory of partial differential equations, it follows that the complete solution is the sum of all the functions $\Phi(u,v,\lambda)$ for all physically acceptable values of λ. In the particular case, however, only one solution is possible. Actually, we argue that the only physically acceptable value for β (and by inference for η) is zero. That it is so becomes clear if eq 47 has to be normalized for all possible values of the parameters a and b (e.g., $a = 1$ and/or $b = -1$). Accordingly, only one value of the separation constant $\lambda = (\rho_v k_v)/\gamma_v$ gives physically acceptable solutions.

After imposing the boundary conditions and transforming the (u,v) variables back into (ζ,ξ) coordinates, the following solution results

$$\Psi(\zeta,\xi) = \exp\{C_\zeta(\zeta - 1) + C_\xi(\xi - 1)\} \tag{48}$$

where

$$C_\zeta = b(\rho_u/\gamma_u) + \rho_v/\gamma_v \tag{48a}$$

$$C_\xi = \rho_u/\gamma_u - a(\rho_v/\gamma_v) \tag{48b}$$

Equation 48 is recognizable as the product of the generating functions for two distinct Poisson distributions. From this result for $\Psi(\zeta,\xi)$, it immediately follows that

$$N_{r,i-r} = \frac{1}{i!}\binom{i}{r}C_\zeta{}^r C_\xi{}^{i-r} \exp\{-(C_\zeta + C_\xi)\} \tag{49}$$

$$\bar{n}_A = (\partial\Psi/\partial\zeta)_{\zeta=\xi=1} = C_\zeta; \qquad \bar{n}_B = (\partial\Psi/\partial\xi)_{\zeta=\xi=1} = C_\xi \tag{50a}$$

$$\bar{n}_{tot} = (1 + b)\frac{\rho_u}{\gamma_u} + (1 - a)\frac{\rho_v}{\gamma_v} \tag{50b}$$

Moreover, the distribution of locus population with respect to the overall number of radical occupancy i is still Poissonian

$$N_i = \sum_{r=0}^{i} N_{r,i-r} = \frac{1}{i!}(C_\zeta + C_\xi)^i \exp\{-(C_\zeta + C_\xi)\} = \frac{1}{i!}(\bar{n}_{tot})^i \exp\{-\bar{n}_{tot}\} \tag{51}$$

This is further substantiated by considering that in the (ζ,ξ) plane, along the line $\vec{\tau}$ defined by $\tau = \zeta$ and $\tau = \xi$, the generating function $\Psi(\zeta,\xi)$ for copolymers should reduce itself to the corresponding one for homopolymers[5]

$$\Psi(\vec{\tau}) = \exp\left\{\frac{\bar{\rho}}{\bar{k}}(\vec{\tau} - 1)\right\} \tag{52}$$

where $\bar{\rho}$ and $\bar{k}$ are the pseudohomopolymerization rate parameters for radical entry and radical exit. By this method, it is possible to determine without any loss of accuracy the mixing rules for the pseudohomopolymerization approach relative to the rate constants of radicals A and B. For elementary events that are zero order with respect to radical concentration within the latex particles, i.e., radical entry, the overall rate constant is simply the sum of the single rate parameters. Actually, for the particular case in which $k_A = k_B = k$, from eq 39 we have

$$a = 1; \qquad \rho_u = \rho_A + \rho_B; \qquad \gamma_u = \frac{(\gamma_A + \gamma_B)}{\gamma_A}k \tag{53}$$

so that

$$\bar{n}_{tot} = \bar{\rho}/k = (\rho_A + \rho_B)/k \tag{54}$$

However, as already pointed out, for most systems of practical interest we have $\gamma_i \gg k_i$ (i = A, B) so that $a = 1$ and

$$\bar{n}_{tot} = (\rho_A + \rho_B)/k^*$$

where k^* is a suitable mean of the single rate constants for radical exit. It is easily proven by this approach that k^* coincides with the rate constant $\bar{k}$ in the pseudohomopolymerization approach (eq 16b):

$$k^* = \frac{\gamma_A k_B + \gamma_B k_A}{(\gamma_A + \gamma_B)} = \bar{k} \tag{55}$$

Finally, it has to be pointed out that the distribution function of reaction loci having an overall number i of growing radicals, but a different ratio between radicals of type A and B, is still binomial.

$$P_{r,i-r} = \frac{N_{r,i-r}}{\sum_r N_{r,i-r}} = \binom{i}{r}\frac{C_\zeta{}^r C_\xi{}^{i-r}}{(C_\zeta + C_\xi)^i} = \binom{i}{r}x_A{}^r(1 - x_A)^{i-r} \tag{56}$$

where $x_A = \bar{n}_A/\bar{n}_{tot}$ is the number fraction of growing radicals of type A present in the system.

In the non-steady state, setting $c_{AA} = c_{BB} = c_{AB} = 0$, the partial differential equation to be solved for $\Psi(\zeta,\xi,t)$ is

$$\partial\Psi/\partial t = -[\rho_A(1 - \zeta) + \rho_B(1 - \xi)] + [k_A(1 - \zeta) + \gamma_A(\xi - \zeta)]\partial\Psi/\partial\zeta + [k_B(1 - \xi) + \gamma_B(\zeta - \xi)]\partial\Psi/\partial\xi \tag{57}$$

By means of eq 36 and 38, eq 57 can be readily transformed into

$$\partial\Phi/\partial t = -[\rho_u/\gamma_u(k_u - \gamma_u u) + \rho_v/\gamma_v(k_v - \gamma_v v)]\Phi + 1/C\{(k_u - \gamma_u u)\partial\Phi/\partial u + (k_v - \gamma_v v)\partial\Phi/\partial v\} \tag{58}$$

It is now possible to show that the solution to eq 57 appropriate to the reaction system under examination is

$$\Phi = A\exp\{-C[\rho_u/\gamma_u{}^2(k_u - \gamma_u u)\alpha(t) + \rho_v/\gamma_v{}^2(k_v - \gamma_v v)\beta(t)]\} \tag{59}$$

where A is a normalization constant and $\alpha(t)$ and $\beta(t)$ are only a function of time. Since for $t = \infty$ eq 59 must converge to eq 47, it follows that

$$\lim_{t\to\infty} \alpha(t),\ \beta(t) = 1 \tag{60a}$$

$$\lim_{t\to\infty} \mathrm{d}\alpha(t)/\mathrm{d}t,\ \mathrm{d}\beta(t)/\mathrm{d}t = 0 \tag{60b}$$

Moreover, the initial boundary conditions state that $\alpha(0) = \beta(0) = 0$ because $\Psi(\zeta,\xi,0) = 1$. By substituting eq 59 into eq 58 one obtains

$$-C/\gamma_u\ \mathrm{d}\alpha(t)/\mathrm{d}t + 1 - \alpha(t) = \rho_u/\gamma_u\lambda/(k_u - \gamma_u u) \tag{61a}$$

$$-C/\gamma_v\ \mathrm{d}\beta(t)/\mathrm{d}t + 1 - \beta(t) = \rho_v/\gamma_v\lambda/(k_v - \gamma_v v) \tag{61b}$$

where λ is a separation constant.

We note here that a true variable separation has not been achieved. However, the initial boundary conditions for $\alpha(t)$ and $\beta(t)$ are satisfied only for $\lambda = 0$. Accordingly, $\alpha(t)$ and $\beta(t)$ are given by the following expressions:

$$\alpha(t) = 1 - \exp[-(\gamma_u/C)t] \tag{62a}$$

$$\beta(t) = 1 - \exp[-(\gamma_v/C)t] \tag{62b}$$

By imposing the normalization condition and returning to ζ,ξ variables, we have

$$\Psi(\zeta,\xi,t) = \exp\{[(\rho_u/\gamma_u)b\alpha(t) + (\rho_v/\gamma_v)\beta(t)](\zeta - 1) + [(\rho_u/\gamma_u)\alpha(t) - a(\rho_v/\gamma_v)\beta(t)](\xi - 1)\} = \exp\{C_\zeta(t)(\zeta - 1) + C_\xi(t)(\xi - 1)\} \tag{63}$$

The function $\Psi(\zeta,\xi,t)$ is the product of two generating functions for a Poisson distribution whose parameters are $C_\zeta(t)$ and $C_\zeta(t)$.

Through the function $\Psi(\zeta,\xi,t)$ it is possible to obtain expressions, in the non-steady-state, for the distribution function $P_{r,i-r}(t)$ of reaction loci having an overall number i of growing radicals. As shown in a preceding section, this result is not attainable through the pseudohomopolymerization approach. From the definition of $P_{r,i-r}(t)$ we have

$$P_{r,i-r}(t) - N_{r,i-r}(t)/\sum_{r=0}^{i} N_{r,i-r}(t) = \binom{i}{r}x_A(t)^r(1 - x_A(t))^{i-r} \tag{64}$$

where

$$x_A(t) = \frac{C_\zeta(t)}{C_\zeta(t) + C_\xi(t)} = \frac{(\rho_u/\gamma_u)b\alpha(t) + (\rho_v/\gamma)\beta(t)}{(1 + b)(\rho_u/\gamma_u)\alpha(t) + (1 - a)(\rho_v/\gamma_v)\beta(t)} \tag{65}$$

is the number fraction of radicals of type A. As shown, a binomial distribution function is found also for the non-steady state.

It may be interesting to examine the very first reaction times. From eq 28 and 63 we have

$$\lim_{t\to 0} \bar{n}_A(t) = 1/C[b\gamma_u + \gamma_v]t = \rho_A t \tag{66a}$$

$$\lim_{t\to 0} \bar{n}_B(t) = 1/C[\gamma_u - a\gamma_v]t = \rho_B t \tag{66b}$$

and, as a consequence

$$\lim_{t\to 0} x_A(t) = \rho_A/(\rho_A + \rho_B) \tag{67}$$

Such a result could be deduced by simple qualitative reasoning. Actually, in the early stages of an emulsion copolymerization reaction, the only elementary event relevant to the loci distribution is radical entry. Moreover, only particles having zero or one growing radical should exist, so that the number fraction of radicals of type A or B depends only on the relative probability of the specific entry rate constants. The correctness of the limiting behavior of the time dependent $\alpha(t)$ and $\beta(t)$ functions represents a probe for the theoretical soundness of eq 63.

Comparison between the Present and the Previous Results

Up to now, in the scientific literature, the kinetics of emulsion copolymerizing systems has been analyzed by applying the so-called "instantaneous termination" approach.[13,19] In this method it is assumed that $\bar{c} \gg \bar{\rho}, \bar{k}$, so that negligibly few particles contain two or more free radicals because of the rapidity of the bimolecular termination reaction. This approximation holds true for many systems of practical interest, e.g., styrene/MMA. With the simplification that only particles containing zero or one free radical need be considered, the steady-state value $\bar{n}_{\text{tot}}$ of the average number of radicals per particle is given by

$$\bar{n}_{\text{tot}} = \frac{\bar{\rho}}{2\bar{\rho} + \bar{k}} \qquad (68)$$

This means that under conditions of instantaneous termination $\bar{n}_{\text{tot}}$ is always less than or equal to $^1/_2$. On the other hand, in the approach presented in the previous section it is assumed that $\bar{\rho}$, $\bar{k} \gg \bar{c}$ so that bimolecular chain-stopping events can be safely ignored. According to this model, it follows that[5]

$$\bar{n}_{\text{tot}} = \bar{\rho}/\bar{k} \qquad (69a)$$

$$N_i = \frac{1}{i!}\bar{n}_{\text{tot}} \exp(-\bar{n}_{\text{tot}}) \qquad (69b)$$

Depending on the relative importance of entry versus exit reactions, $\bar{n}_{\text{tot}}$ may range from zero to $\bar{n}_{\text{tot}} \gg {}^1/_2$ in the limit $\bar{\rho} \gg \bar{k}$. Correspondingly, particles containing only one growing radical become negligible. Apparently in this approach it is impossible to account for systems where $\bar{n}_{\text{tot}} \leqslant {}^1/_2$ and $\bar{c} \gg \bar{\rho}, \bar{k}$. However, this apparent restriction can be easily lifted by simple physical reasonings.

For a system where $\bar{c} \gg \bar{\rho}, \bar{k}$, a free radical entering a latex particle containing i growing polymer radicals causes this particle to increase by unit its "radical state of occupancy".[12] The mean residence time τ of the particle in state $i + 1$ is very short since $\bar{c}$ is very large. At time $\tau + dt$ the state of the particle is $i - 1$. During this time interval two radicals lost their activity: one free radical (the one that caused the latex particle to change its state) and one polymer radical. Moreover, if we assume that $\bar{c}$ is such that $\tau < 1/k_{\text{P}}C_{\text{M}}$ (where C_{M} is the overall monomer concentration), the polymer radical remains unchanged in length during all this period. Were we not aware of bimolecular termination reactions, we might assume that the polymer radical lost its activity by a monomolecular reaction concomitant with radical entry.

The overall sequence of these elementary reactions (including the time τ the particle spent in state $i + 1$) can be accounted for in eq 69a and 69b by substituting $\bar{k}$ by a new exit pseudoconstant $\bar{\chi}$ defined as

$$\bar{\chi} = \bar{k} + 2\bar{\rho} \qquad (70)$$

The factor 2 in eq 70 accounts for the death of two distinct radicals. It is worth noting that by this method we have assumed only $\bar{c} \gg \bar{\rho}, \bar{k}$ whereas in the instantaneous termination approach the truncation of the allowed states at $i = 1$ implicitely entails $\bar{c} = \infty$. Obviously this assumption has no physical meaning. The only difference between the zero-one system and the approach proposed here for treating systems where $\bar{n}_{\text{tot}} \leqslant {}^1/_2$ is the particle state distribution, $\bar{n}_{\text{tot}}$ being exactly the same.

By introducing the new exit rate constants $\chi_{\text{i}} = k_{\text{i}} + 2\rho_{\text{i}}$ (i = A, B), the extension of this method to emulsion copolymerization is straightforward in the pseudohomopolymerization approach. It is not so in the most general case. However, for systems where c_{ij}, $c_{\text{ii}} \gg \rho_{\text{i}}$, k_{i} (i, j = A, B; i $\neq$ j), a close inspection of the analytic expressions of $\bar{n}_{\text{A}}$ and $\bar{n}_{\text{B}}$, both in the stationary and nonstationary state, shows that they result from a linear combination between ρ_u/γ_u and ρ_v/γ_v. In addition, both ρ_j and γ_j ($j = u, v$) are linear combinations of ρ_{i} and k_{i} (i = A, B). By analogy, applying the same previous reasonings, for systems where bimolecular termination is overwhelming with respect to radical entry and exit, in the most general case, k_{i} needs to be substituted by $(2\rho_{\text{i}} + k_{\text{i}})$ (i = A, B) and ρ_j/γ_j by $\rho_j/(2\rho_j + \gamma_j)$ ($j = u, v$).

Table II
Rate Coefficients Used in Calculations[a] and the Average Numbers of Radicals per Particle, $\bar{n}_{\text{A}}$ and $\bar{n}_{\text{B}}$, for Styrene/MMA and Styrene/Butadiene Emulsion Copolymerization Systems

	A (styrene)	B (MMA)	B (butadiene)
ρ_{A}, ρ_{B} (s^{-1})	1×10^{-4}	4×10^{-3}	1×10^{-3}
k_{A}, k_{B} (s^{-1})	1.5×10^{-3}	1×10^{-3}	1×10^{-3}
$k_{\text{p,AB}}$, $k_{\text{p,BA}}$ (L mol^{-1} s^{-1})	496	1076	40
$k_{\text{tr,AB}}$, $k_{\text{tr,BA}}$ (L mol^{-1} s^{-1})	0.12	0.08	0.06
C_{MA}, C_{MB} (mol L^{-1})			
MMA as comonomer	4	3	
butadiene as comonomer	3		2
$\bar{n}_{\text{A}}$, $\bar{n}_{\text{B}}$			
MMA as comonomer	0.315,[b] 0.318[c]	0.109,[b] 0.110[c]	
Butadiene as comonomer	0.038,[b] 0.037[c]		0.317,[b] 0.312[c]

[a] Data from ref 13. [b] Pseudohomopolymerization approach. [c] Rigorous approach.

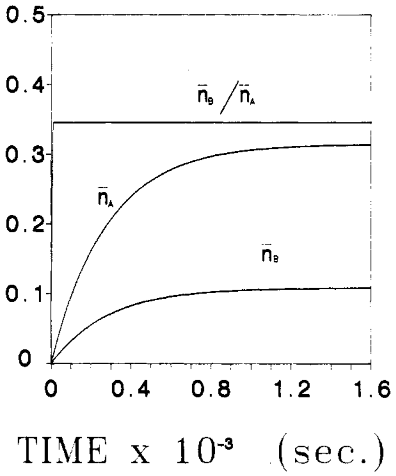

Figure 3. Radical number fractions ($\bar{n}_{\text{A}}$ and $\bar{n}_{\text{B}}$) and instantaneous radical ratio $\bar{n}_{\text{B}}/\bar{n}_{\text{A}}$ as functions of time for styrene/MMA (A/B): kinetic parameters from Table II.

Although not stemming from a rigorous theoretical footing, this approach provides correct results. In Table II we report the evaluation of $\bar{n}_{\text{i}}$ (i = A, B), both by the pseudohomopolymerization approach and in the most general case, for two systems of practical interest where $\bar{n}_{\text{tot}} \leqslant {}^1/_2$. In Figure 3 we show also solutions in the nonstationary state for a seeded styrene/MMA copolymerization. Also shown is the time dependence of the instantaneous radical composition $\bar{n}_{\text{B}}(t)/\bar{n}_{\text{A}}(t)$. These results compare well with the estimate of Ballard et al.[13] based on numerical solutions of the SE equations.

Conclusions

This paper develops a comprehensive description of the time evolution of the locus population distribution of emulsion copolymerizing systems. Based on an extended SE theory, time-dependent equations are derived for latex particles containing r growing radicals of type A and $i - r$ radicals of type B, where i may range from 1 to infinity. All population-changing elementary events are accounted for within a simple population balance framework. By applying an appropriate two-variable transform, the infinite set of differential difference equations reduces to a single, highly symmetrical, linear partial differential equation of the second order. This proposed "wave equation" corresponds to the well-known Stockmayer–O'Toole[14,18] equation for emulsion homopolymers. This is a very remarkable result. Actually, by solving only one differential equation, it is possible to find the locus population generating function $\Psi(\zeta,\xi,t)$. All the information concerning the distribution of locus populations is encapsulated in the function Ψ: hence the term "wave equation".

Central to this approach is the introduction of a particular combination of a two-variable power transform: a simple power transform and an inverse one. Only by this method a relatively simple generating function equation results. Moreover, it is possible to make inferences concerning the analytic form of the related solution. Actually, along the diagonal in the plane region where $\Psi(\zeta,\xi,t)$ is defined, it must reduce to the corresponding generating function for homopolymers. In this connection, it is shown that for copolymerizing systems where the bimolecular termination is not relevant with respect to the other elementary reactions, the generating function $\Psi(\zeta,\xi,t)$ is the product of two Poisson distribution functions. This enables one to determine exactly the mixing rules between the rate parameters of radicals of type A and radicals of type B to give pseudohomopolymerization rate constants. On these grounds, we can conclude that the pseudohomopolymerization approach, developed in a previous paper in this series,[12] satisfactorily accounts for the kinetics of compartmentalized free-radical copolymerizations.

In contrast to emulsion homopolymerizations where stationary-state solutions contain only ordinary differential equations, the "wave equation" for emulsion copolymers is a partial differential equation also for stationary-state systems. In this connection, considerable difficulty is experienced in obtaining an explicit analytic solution to the completely general eq 32. The difficulties in dealing with these partial differential equation systems have two main sources. One is the unsatisfactory state of the general analytic theory of partial differential equation systems. The other is our very scant knowledge of the behavior of solutions in the neighborhood of points at which more than two singular curves of the system intersect. However, it is possible to demonstrate that, for a few very distinctive cases, the stationary state solution takes the form of two-variable hypergeometric functions (Horn's functions). This notwithstanding, giving the present state of sophistication, when developing solutions for the completely general steady-state equations, it is necessary to resort to approximation procedures.

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