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Emulsion Polymerization: Improved Methods for Solving the Smith–Ewart Equations in the Unsteady State

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ABSTRACT: A simplified procedure for calculating the average number of radicals per particle, $\bar{n}(t)$, in an emulsion polymerization is discussed. The methodology may be used for a fixed number of particles in the unsteady state. Comparison with previously reported treatments is made. It is shown that this method can be used over all the range of possible conditions with negligible error. Checking for precision against an exact numerical solution shows a high degree of accuracy. In this procedure allowance can be easily made for the dependence of the various rate constants on particle size.

Introduction

Even though recent years have been marked by considerable advances, a comprehensive description of emulsion polymerization has not yet been achieved. Whereas the elementary steps of chain growth are essentially those of homogeneous bulk or solution polymerization, in an emulsion system the segregation of the propagating radicals into latex particles physically isolates them from each other in very small groups. The main consequence of this compartmentalization effect is that the probability of mutual termination is reduced relative to the case of a similar polymerization occurring in a homogeneous medium at the same overall concentration of growing species. The kinetic behavior of these two reacting systems should be therefore quite different. This applies especially when the number of separate reaction loci (latex particles) is of the same order of magnitude as the number of propagating free radicals. It therefore follows that the average number of radicals per single reaction locus, $\bar{n}$, is small. Usually 10 is regarded as the upper limit beyond which conventional homogeneous kinetics can be applied without error and 0.01–2 as the range that covers many systems of practical interest.

The fundamental equations describing the kinetics of an emulsion free-radical polymerization were proposed by Smith and Ewart[1] (SE) more than 40 years ago. For a system where the number density of latex particles is assumed to remain constant over the reaction time (interval II), the following set of population balance equations results:

$$\mathrm{d}N_i/\mathrm{d}t = \rho[N_{i-1} - N_i] + k[(i+1)N_{i+1} - iN_i] + c[(i+2)(i+1)N_{i+2} - i(i-1)N_i] \quad (1)$$

where

$$\sum_{i=0}^{\infty} N_i = 1$$

Here N_i represents the relative number of latex particles containing i free radicals, ρ is the pseudo-first-order rate coefficient for entry of free radicals into latex particles, k is the first-order rate coefficient for loss of a single free radical from the latex particles, and $2c$ is the pseudo-first-order rate coefficient for mutual annihilation between two growing radicals.

An exact steady-state solution was first obtained by Stockmayer[2] and subsequently modified by O'Toole.[3] By contrast, in the unsteady state up to now general solutions to the SE equations have been elusive, although a number of approximate solutions have appeared in the scientific literature over the last 15 years. Most of these approximation procedures[4–6] provide reasonable results over a limited range of conditions only ($\bar{n} \leq 0.4$). In these treatments the infinite set of differential difference equations is truncated very early so that only latex particles having no more than one or two growing radicals are taken into account. This truncation inevitably introduces a distortion into the set of the obtained equations. The error becomes negligible only if the maximum number of radicals taken into account is large enough to correctly describe the kinetic behavior of the system being represented. An alternative approach was proposed by Blackley[7] and subsequently revised by Song and Pohelein.[8] The SE equations were approximated by a new set of equations. It was shown that the approximation holds true provided that the dominant radical loss mechanism is not second order. For systems not conforming to the above mentioned restrictions (low $\bar{n}$ and $k > c$), numerical solutions are needed. However, the SE equations are stiffly coupled so that appropriate algorithms, like the Gear[9] method or more sophisticated finite difference schemes like the implicit Crank–Nicolson[10] approach, are required. As a consequence, the lack of any general analytic solution for the time-dependent kinetics of emulsion polymerization prevented the development of simple models for the predictions of important product properties of these reacting systems (for example, conversion of monomers) or the development of simplified models devised for process simulation. The purpose of this paper is to overcome this limitation and to provide closed analytic solutions to the time-dependent SE equations giving satisfactory representation of reality over all the space of values of the involved kinetic constants (ρ, k, and c). For the sake of simplicitly, in this treatment ρ is the overall first-order rate coefficient for entry of free radicals, including any effect due to reentry and heterotermination in the aqueous phase of exited radicals.

Theoretical Framework

The SE equations belong to a particular kind of stochastic process encountered very often in relation to problems of population "birth and death".[11] One of the most successful methods for a complete solution of generalized birth-and-death processes involves replacing the differential difference equations for the distribution of the population size by a partial differential equation for its generating function. For an account of this technique in relation to emulsion polymerization, reference may be made to Blackley's work.[7] For transient processes

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where the number density of latex particles remains constant with time, the following partial differential generating equation is found:

$$\partial\Psi/\partial t = \rho(x-1)\Psi + k(1-x)\partial\Psi/\partial x + c(1-x^2)\partial^2\Psi/\partial x^2 \quad (2)$$

where $\Psi(x,t) = \sum_{i=0}^{\infty} N_i(t)x^i$. So far it has not been possible to give an entirely general solution to eq 2. However, as far as only the kinetic behavior of the reacting system is involved, a limited number of information about the $N_i(t)$ distribution is required. Actually, for a compartmentalized free-radical polymerization, the overall rate of polymerization may be written as

$$\mathrm{d}M/\mathrm{d}t = (N_C/N_A)k_p[M]_p\bar{n}(t) \quad (3)$$

where M are the moles of monomer converted per unit volume of water, N_C is the number of latex particles per unit volume of water, N_A is Avogadro's number, k_p is the rate coefficient for propagation, $[M]_p$ is the concentration of the monomer in the particles, and $\bar{n}(t)$ is the average number of propagating radicals per reaction locus. It is therefore only the first moment of the $N_i(t)$ distribution that is of interest. To this end, some useful mathematical devices were developed by Kendall[12] for the treatment of generalized birth-and-death processes. The first one was the introduction of the functional

$$\mathbf{M}(u,t) \equiv \Psi(e^u,t) \quad (4)$$

In the neighborhood of $u = 0$ the $\mathbf{M}(u,t)$ function behaves as the generating function of the moments of the $N_i(t)$ distribution. Actually, by expanding the exponential e^u and from the definition of the rth moment $\mu_r(t)$, we have

$$\mathbf{M}(u,t) = \sum_{r=0}^{\infty}\mu_r(t)\frac{u^r}{r!} \quad (5a)$$

$$(\partial^r\mathbf{M}/\partial u^r)_{u=0} = \mu_r(t) \quad (5b)$$

Applying the variable change $x = e^u$ to eq 2 then gives

$$\partial\mathbf{M}/\partial t = \rho(e^u-1)\mathbf{M} + (e^{-u}-1)[k-(1+e^u)c]\frac{\partial\mathbf{M}}{\partial u} + c(e^{-2u}-1)\frac{\partial^2\mathbf{M}}{\partial u^2} \quad (6)$$

Finally, expanding both sides of eq 6 in powers of u and equating the coefficients, one obtains the differential equations for the time evolution of the moments:

$$\frac{\mathrm{d}\mu_i}{\mathrm{d}t} = \sum_{j=2}^{i}\left\{\binom{i}{j}\rho + k\binom{i}{j-1}(-1)^{i-j+1} + c\left[\binom{i}{j-2}(-2)^{i-j+2} - \binom{i}{j-1}(-2)^{i-j+1}\right]\right\}\mu_j + (i\rho + k(-1)^i - c(-2)^i) + \rho(1-\mu_i) - 2ic\mu_{i+1} \quad (7)$$

In particular, the time-dependent equations relative to the first two moments are

$$\mathrm{d}\mu_1/\mathrm{d}t = \rho - k\mu_1 - 2c(\mu_2 - \mu_1) \quad (7a)$$

$$\mathrm{d}\mu_2/\mathrm{d}t = \rho + (2\rho + k - 4c)\mu_1 + 2(4c - 2k)\mu_2 - 4c\mu_3 \quad (7b)$$

The derived equations comprise an infinite set of "open" linear ordinary differential equations: e.g., any moment $\mu_i(t)$ $(i > 0)$ is coupled to all other moments $\mu_j(t)$ $(j < i)$ and to $\mu_{i+1}(t)$.

The second device that has been proposed is the cumulant generating function defined by the functional

$$\mathbf{K}(u,t) \equiv \ln[\Psi(e^u,t)] \quad (8)$$

The function $\mathbf{K}(u,t)$ can be expanded in the neighborhood of $u = 0$ in terms of the cumulants $k_r(t)$:

$$\mathbf{K}(u,t) = \sum_{r=1}^{\infty}k_r(t)\frac{u^r}{r!} \quad (9a)$$

$$(\partial^r\mathbf{K}/\partial u^r)_{u=0} = k_r(t) \quad (9b)$$

Applying the functional in eq 8 to the time-dependent SE generating eq 2, we have

$$\partial\mathbf{K}/\partial t = \rho(e^u-1)\mathbf{K} + k(e^{-u}-1)\frac{\partial\mathbf{K}}{\partial u} + c(e^{-2u}-1)\left[\left(\frac{\partial\mathbf{K}}{\partial u}\right)^2 - \frac{\partial\mathbf{K}}{\partial u} + \frac{\partial^2\mathbf{K}}{\partial u^2}\right] \quad (10)$$

Again, expanding both sides in powers of u and equating the coefficients, we obtain a set of differential equations for the time evolution of the cumulants:

$$\frac{\mathrm{d}k_i}{\mathrm{d}t} = \rho + i!\,k\left[\sum_{j=1}^{i}\frac{k_j}{(j-1)!}\frac{(-1)^{i-j+1}}{(i-j+1)!}\right] + i!\,c\left[\sum_{j=2}^{i+1}\frac{a_j(-2)^{i+2-j}}{(i+2-j)!}\right]$$

$$a_j = \sum_{l=1}^{j-1}\left[\frac{k_lk_{j-l}}{(l-1)!(j-l-1)!}\right] + \frac{1}{(j-2)!}[k_j - k_{j-1}] \quad (11)$$

The first two equations are

$$\mathrm{d}k_1/\mathrm{d}t = \rho + (2c-k)k_1 - 2ck_1^{\,2} - 2ck_2 \quad (11a)$$

$$\mathrm{d}k_2/\mathrm{d}t = \rho + k_1(k-4c) + 4ck_1^{\,2} - 8ck_1k_2 + 2k_2(4c-k) - 4ck_3 \quad (11b)$$

Also in this case, the resulting time-dependent equations comprise an infinite set of open differential equations. However, in contrast to the moment equations, the cumulant equations are not linear. It is worth noting that, since $k_1 = \bar{n}$ and $k_2 = \sigma^2$ (where σ^2 is the variance), from eq 11a we have

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho - k\bar{n} - 2c(\bar{n}^2 - \bar{n} + \sigma^2) \quad (12)$$

which is the equation previously derived by Ballard et al.[13]

Solutions of the Time-Dependent Moment and Cumulant Equations

The solution of an infinite set of open differential equations requires an appropriate truncation at a finite number. However, contrary to the case of the SE equations, where the truncation at a given index i is made possible since at that value the fraction of reaction loci that contain more than this number of propagating radicals is negligible, this is not allowed for both the moment and the cumulant equations. Since we are interested only in solving the first time-dependent equation out of the whole set, truncation must be applied at this level. To this end, as a *first-order* approximation, we suppose that the ratio between contiguous moments is time independent. Under this assumption, eq 7a may be rewritten as

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho - \{k + 2c[(M_{21})_{ss} - 1]\}\bar{n} \tag{13}$$

where $(M_{21})_{ss}$ is the ratio between the second and the first moment of the $N_i(t)$ distribution at steady state. $(M_{21})_{ss}$ can be evaluated from the steady-state solution of eq 2 according to the following expression:

$$(M_{21})_{ss} = \left(\frac{h}{4}\right)\frac{I_{m+1}(h)}{I_m(h)} + 1 \tag{14}$$

where $h^2 = 8\alpha$, $\alpha = \rho/c$, $m = k/c$, and $I_m(h)$ is a modified Bessel function of order m. Furthermore, making use of the relationships of contiguous Bessel functions, we have

$$[(M_{21})_{ss} - 1] = \frac{1}{2}\left(\frac{\alpha}{\bar{n}_{ss}} - m\right) \tag{15}$$

where

$$\bar{n}_{ss} = \left(\frac{h}{4}\right)\frac{I_m(h)}{I_{m-1}(h)} \tag{16}$$

$\bar{n}_{ss}$ can be easily evaluated by using the continued fraction method.[14] Recasting eq 13 with eq 15 we have

$$\frac{\mathrm{d}\bar{n}}{\mathrm{d}t} = \frac{\rho}{\bar{n}_{ss}}(\bar{n}_{ss} - \bar{n}) \tag{17}$$

After integration the following equation results:

$$\bar{n}(t) = \bar{n}_{ss}\left(1 - \exp\left[-\frac{\rho}{\bar{n}_{ss}}t\right]\right) \tag{18}$$

Clearly the steady-state value of eq 18 is $\bar{n}_{ss}$, the Stockmayer–O'Toole (SO) value.

The same reasonings can be applied to the first cumulant eq 11a. In this case the steady-state ratio between the first two cumulants is

$$(K_{21})_{ss} = (M_{21})_{ss} - \bar{n}_{ss} \tag{19}$$

Recasting eq 11a with eq 15 and eq 19, we finally have

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho + (2c\bar{n}_{ss} - \rho/\bar{n}_{ss})\bar{n} - 2c\bar{n}^2 \tag{20}$$

In this case, contrary to eq 13, the time evolution equation of the $\bar{n}(t)$ is not linear. Moreover it is worthwhile noting that the linear term of eq 20 is always negative. Actually for a compartmentalized free-radical polymerization

$$\bar{n}_{ss} \leqslant (\rho/2c)^{1/2} = \bar{n}_{\mathrm{bulk}} \tag{21}$$

Physically the coefficient of the linear term is related to the difference between the steady-state concentration of radicals of the compartmentalized system and an equivalent bulk system where ρ and c denote the rate coefficients for radical creation and mutual annihilation, respectively. The solution of eq 20 subjected to the boundary condition $\bar{n}(0) = 0$ is

$$\bar{n}(t) = 2\rho\frac{\tanh(bt/2)}{b + \chi\tanh(bt/2)} \tag{22}$$

where $b^2 = 8\rho c + \chi^2$, and $\chi = (\rho/\bar{n}_{ss} - 2c\bar{n}_{ss})$. Now, we note here that the assumption of M_{21} and K_{21} independent of time may be a crude one for both eq 7a and eq 11a. Actually, as shown in Figure 1, they are time-dependent functions. Accordingly, a *second-order* approximation should be a certain time dependence also for the cumulants and moments ratio. Hereafter the treatment is presented for the $\mu_2(t)/\mu_1(t)$ ratio. To this end, it is worth pointing out that eq 22 has the same functional form as the approximate "Poissonian" solution given by Blackley[7] to the $\Psi(x,t)$ generating function.

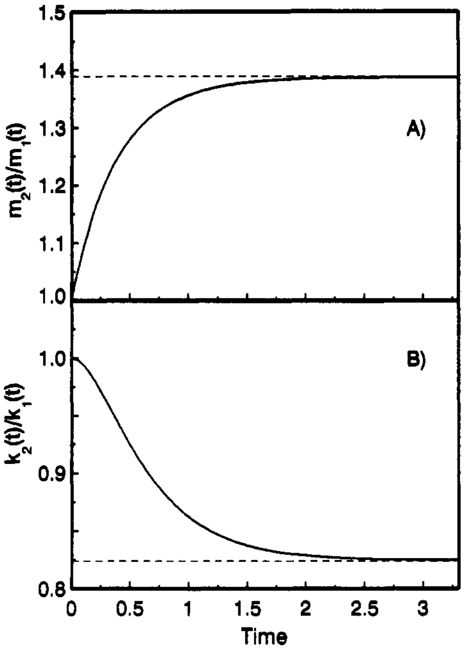

Figure 1. Ratio between the first two contiguous moments (A) and cumulants (B) as a function of time (arbitrary units) for a reaction system for which $\rho = k = c = 1$. Also shown by the dotted lines are the steady-state values.

$$\Psi(x,t) = \exp\{(x - 1)\theta(t)\} \tag{23}$$

$$\theta(t) = 2\rho\frac{\tanh(at/2)}{a + k\tanh(at/2)} \tag{24}$$

where $a^2 = 8\rho c + k^2$. If the $N_i(t)$ distribution is Poissonian, then we shall have at any time

$$[M_{21}(t) - 1] = \theta(t) \tag{25}$$

In this connection, given the close analogy between eq 22 and eq 24, it seems likely that, even if the exact solution of eq 2 is not Poissonian, the ratio between the two first contiguous moments behaves in such a way at any time. If true, we are allowed to write

$$[M_{21}(t) - 1] = [(M_{21})_{ss} - 1]\theta_N(t) \tag{26}$$

where $\theta_N(t)$ is an appropriate normalized Poissonian function; e.g., $\theta_N(0) = 0$ and $\theta_N(\infty) = 1$. The most obvious $\theta_N(t)$ function may be derived directly from eq 22.

$$\theta_N(t) = (b + \chi)\frac{\tanh(bt/2)}{b + \tanh(bt/2)} \tag{27}$$

As shown in Figure 2, numerically this equation provides a reasonable approximation to the exact solution. Furthermore eq 27 may be justified also on the grounds of some theoretical results, since it is possible to demonstrate that the exact solution of the time-dependent generating function is expressible in terms of an infinite summation of hyperbolic functions.[15]

The time evolution of the average number of radicals per latex particle is finally given by the following expression:

$$\mathrm{d}\bar{n}/\mathrm{d}t = \rho - \{2c[(M_{21})_{ss} - 1]\theta_N(t) + k\}\bar{n} \tag{28}$$

The same result may be derived by using the second-order approximation for the cumulants ratio. Equation 28 constitutes a simple linear differential equation of first order and first degree. General integral solutions are available. In this particular case, however, integration does not lead to any simple expression.

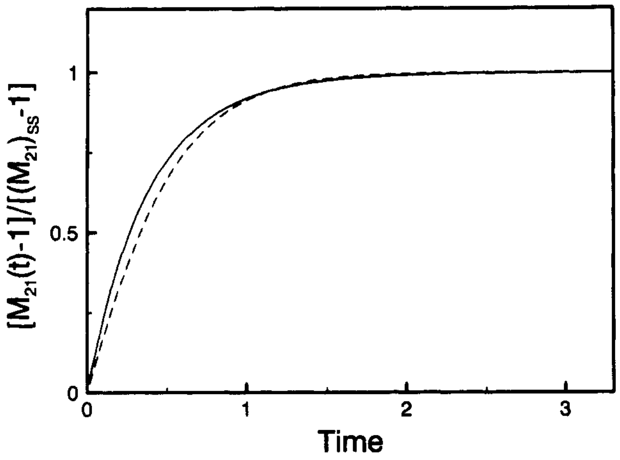

Figure 2. Fractional moment ratio $[M_{21}(t) - 1]/[(M_{21})_{ss} - 1]$ as a function of time (arbitrary units) for a reaction system for which $\rho = k = c = 1$. (- - -) approximate solution from eq 27; (—) exact solution.

Results and Discussion

One of the most well known approximations to the complete set of the SE time-dependent equations is the so called "zero–one" system. In this limit, c is so large that no particle contains more than one free radical for any significant time interval: the conditions are $c \gg \rho, k$. For this two-state model the analysis of experimental data becomes straightforward. It is also possible to obtain analytically the prediction for $\bar{n}(t)$ as a function of time.[5] This approach was extended by Brooks[6] in his three-state model. Explicit expressions were given for the variations of n_1 and n_2 with t, from which $\bar{n}(t)$ can be readily obtained. Both these approximations can be regarded as valid for reaction systems in which $\bar{n}_{ss}$ is small (up to 0.4). Another completely different approach is due to Weiss and Dishon.[4] An analytic solution for $\bar{n}(t)$ was given as a first-order perturbation of the exact solution of eq 2 when $c = 0$. Their results provide good approximation when $\bar{n}_{ss} \ll 1$ and $2\rho c/k^2 > 1$ only.

With the proviso that $k > c$, Blackley[7] was able to demonstrate that an approximate solution of eq 2 subjected to the boundary condition $N_0(0) = 1$ is eq 23. Since this function is the frequency-generating function of a Poissonian distribution, it follows that, under the above mentioned restriction, the distribution of locus populations is Poissonian at all times.

All these treatments seem to fail when the rate constants of the involved elementary reactions are of the same order of magnitude. In this connection, a reaction system where $\rho = k = c$ ($\alpha = 1, m = 1$) should represent the most critical test. For this system $\bar{n}_{ss} = 0.563$, so that at least four states must be taken into account.

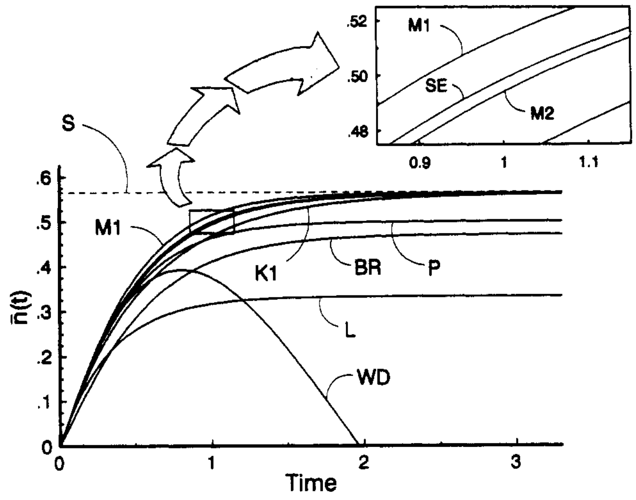

Figure 3. Predictions for $\bar{n}(t)$ as a function of time (arbitrary units) for a reaction system for which $\rho = k = c = 1$ and $\bar{n}_{ss} = 0.563$, as given by the following theories. (i) The Poissonian approximation of Blackley[7] (eq 24, curve P); (ii) the three-state model of Brooks[6] (curve BR); (iii) the two-state model of Lichti et al.[5] (curve L); (iv) the Weiss–Dishon approximation (curve WD); (v) the first-order approximation of the moment ratio (eq 18, curve M1); (vi) the first-order approximation of the cumulant ratio (eq 22, curve K1); (vii) the second-order approximation of the moment ratio (eq 28, curve M2); (viii) the exact numerical solution[10] of the SE equations (curve SE). Also shown by the dotted line is the steady-state value $\bar{n}_{ss}$ as predicted by the Stockmayer–O'Toole theory (eq 16, curve S).

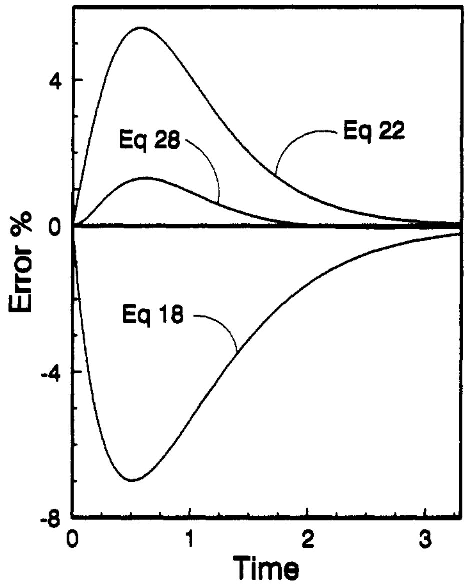

Figure 4. Relative error (%) between the exact and the approximate values of $\bar{n}(t)$ as a function of time (arbitrary units) for a reaction system for which $\alpha = m = 1$.

The results of numerical comparisons between the predictions given by our approximations and the various models discussed above are shown in Figure 3 for the key system $\alpha, m = 1$. Hereafter, the plots of $\bar{n}$ vs t are in arbitrary units. Also given in Figure 3 is the prediction of $\bar{n}_{ss}$ from the SO theory. The most immediate test of the validities of the various approximations for $\bar{n}(t)$ is certainly the accuracy with which they approach the steady-state solution. The "zero–one" model, the three-state model of Brooks, the Poissonian, and the Weiss–Dishon approximations all fail, by various degrees, to approach the SO limit over the long range. On the contrary, all the approximations reported in this paper clearly give the most satisfactory predictions out of those that have been previously investigated. This is true not only in relation to the ability to approach the SO prediction asymptotically, but also in that the fittings at intermediate times are quite accurate. In Figure 4 we report for the three approximate equations the plots of the relative error vs t, where

$$\text{error } \% = [\bar{n}_{\text{appr}}(t) - \bar{n}_{\text{ex}}(t)]/\bar{n}_{\text{ex}}(t) \times 100$$

$\bar{n}_{\text{appr}}(t)$ is the approximate average number of radicals and $\bar{n}_{\text{ex}}(t)$ is the value from the exact solution of the SE eq 1 by a numerical technique.[10] As shown, the first-order approximation (constant M_{21}), applied to both the moment and the cumulant equation, gives satisfactory representations of the behavior of the system, the absolute error being less than 10%. The second-order approximation [Poissonian $M_{21}(t)$] gives results that, from any practical point of view, correspond to the exact kinetic behavior (maximum error is 1.3%). It is worth noting that the

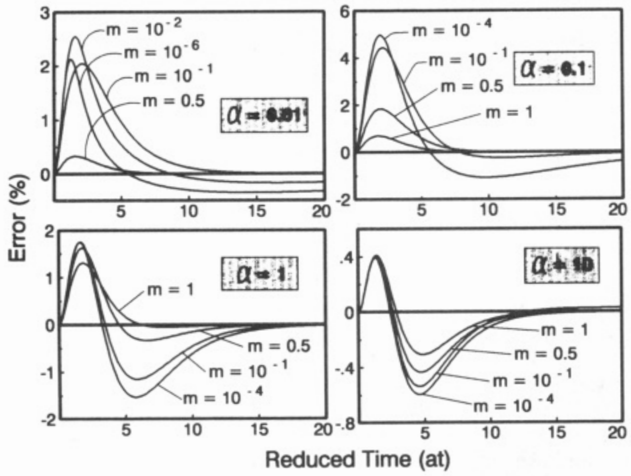

Figure 5. Plots of the relative error (%) between the exact and the approximate values (eq 28) of $\bar{n}(t)$ as a function of the reduced time at for reaction systems for which $\alpha = 0.01$–10 and $m = 10^{-6}$–1.

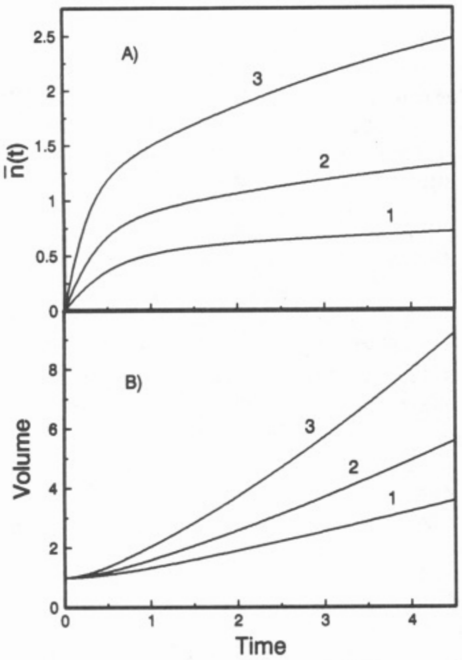

Figure 6. (A) $\bar{n}(t)$ as a function of time (arbitrary units) when ρ, k, and c are given by eq 31 and $K = 1$, $k_0/c_0 = 1$. (B) Particle volume as a function of time. Initial value is $v = 1$. Curve 1: $\rho_0/c_0 = 1$. Curve 2: $\rho_0/c_0 = 2$. Curve 3: $\rho_0/c_0 = 4$.

amount of monomer $M(t)$ converted in a unit volume of the reaction system at time t can be obtained by substituting $\bar{n}(t)$ into eq 3 and then integrating over the range (0–t). In the case of eq 22 a simple analytic result follows:

$$M(t) = \frac{N_C}{N_A}\frac{k_p[M]_p}{2c}\left\{\ln\left[\cosh(bt/2) + \frac{\chi}{b}\sinh(bt/2)\right] - \frac{\chi}{2}t\right\} \quad (29)$$

The first-order approximation also works well for systems where $\alpha > 1$ and $m - \alpha$ ($\bar{n}_{ss} > 0.5$). The reason can be easily understood by inspecting the cumulant eq 22. Here, the higher the $\bar{n}_{ss}$, the lower the value of the linear term ($2c\bar{n}_{ss} - \rho/\bar{n}_{ss}$), so that the system follows closer and closer the pseudobulk kinetics. On the contrary, even if predictions over the long range are satisfactory, when $\alpha \ll 1$ the first-order approximation appears to seriously over- and/or underestimate $\bar{n}(t)$ at earlier reaction times. The second-order approximation in eq 28 overcomes this drawback, representing very closely the exact behavior of the reaction system over all the values of α and m. Figure 5 shows the plots of the relative error (%) as a function of the reduced time at. The SO α parameter was allowed to vary from 10^{-2} to 10 and m from 1 to 10^{-6}. The $\bar{n}_{ss}$ values of the related systems varied from 0.02 to 2.11, covering thus the range of systems of practical interest. As shown, the maximum error is 5% at $\alpha = 0.1$ and $m = 10^{-4}$. However, this error relates to the description of $\bar{n}(t)$ at early reaction times. Basically, this means that the second-order approximation of the moment equation gives plots of $\bar{n}(t)$ that are indistinguishable from the exact solution over all the values of the kinetic parameters.

Equation 28 may also represent a simple, valuable tool for process simulations including some functional dependences of the rate constants on volume. Actually, when the volume of the particles increases during polymerization, in addition to eq 28 and eq 16 we have also

$$\mathrm{d}v/\mathrm{d}t = K\bar{n}(t) \quad (30)$$

where K is the volume growth rate of a particle containing one free radical.[16] For the purpose of comparisons the numerical solutions corresponding to

$$\rho = \rho_0 v^{1/3} \quad (31a)$$

$$k = k_0 v^{-2/3} \quad (31b)$$

$$c = c_0/v \quad (31c)$$

are shown in Figure 6 for three values of ρ_0/c_0 with constant $k_0/c_0 = 1$. In all these cases, when allowance is made for volume dependence of the rate constants, the reaction rate never reaches a constant value.

These results were obtained numerically by solving a set of two linear differential equations. A fourth-order Runge and Kutta method was used. Contrary to the original SE equations, this set of two equations has no stiffness. Moreover, both convergence and stability of the solution are very high.

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