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Comprehensive Theory of Particle Growth in the Smith–Ewart Interval II of Emulsion Polymerization Systems[†]

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ABSTRACT: A mathematical model is developed for describing the time evolution of particle size distribution (PSD) in the Smith–Ewart Interval II of emulsion polymerizations. By use of an appropriate combination of transforms, the infinite set of partial differential difference equations for the time evolution of particle size is transformed into a single partial differential "wave equation". It is shown that all the information connected to the growth history of the reacting polymer latex is encapsulated in this equation. General solutions are presented for systems having an average number of radicals per particle either <0.5 or >0.5. In this treatment the contribution of bimolecular termination reactions is explicitly included. The model provides good fitting to experimentally available PSD data of styrene.

Introduction

Even though the technique has been used in the industry for many years, emulsion polymerization is still attracting a great deal of interest from both industrial and academic laboratories.[1] From a practical viewpoint this technology offers considerable processing advantages over bulk, suspension, or solution free-radical polymerizations. For example, low viscosity of the reacting medium and good temperature control can often be achieved in an emulsion polymerization when this is impossible in bulk. Furthermore, high molecular weight polymers can be obtained at reaction rates considerably higher than those observed for conventional free-radical processes. The methodology leads to the generation of polymer in the form of a latex. This presents unique physical advantages in the manufacture of products such as paints, coatings, adhesives, and others.

From the theoretical point of view, emulsion polymerization still represents a challenging area of endeavor. The heterogeneous nature of the reacting system makes it necessary to take into account reactions in both the dispersing medium and the swollen polymeric phase.

Since the fundamental paper of Smith and Ewart[2] (SE), particle size distribution (PSD) and molecular weight distribution (MWD) have been recognized as the detailed blueprints of the series of elementary reactions that determine the growth history of the emulsion polymerization process. Actually, not only do they influence the properties of the product in end-use applications but they also contain information about the set of rate coefficients for various microscopic events occurring during the reaction. It stands to reason then that the last few years have been marked by considerable efforts in developing more sophisticated mathematical models for the prediction of both these two experimentally available distributions.[1,3] Accordingly, as part of our interest in the theoretical modeling of emulsion reacting systems,[4,5] in this paper we shall address the problem of a comprehensive treatment for the time evolution of the PSD.

Background

The development of the constitutive balance equations for an emulsion polymerization process entails a detailed knowledge of all the microscopic events occurring therein. In this connection it has been recognized for many years[6] that there are two primary factors affecting PSD: particle formation and particle growth. A number of different kinetic models of particle formation in emulsion polymerization are available in the scientific literature.[1,2,7–11] However, only recent works by Australian researchers[1,12] have shed considerable light on the mechanisms whereby latex particles are formed in heterogeneous reacting systems. The proposed model describes the formation of latex particles taking into account the theories of colloid science. For the model systems considered calculations have shown good agreement with experimental data.

On the other hand, the problem of particle growth has been dealt with by different authors. The stochastic broadening of the PSD has been considered in the pioneering work of Ewart and Carr,[6] although only restricted cases were treated. Numerical solutions were also provided by Sundberg and Eliassen[13] by applying the method of the moments. Other authors[9,14,15] quantitatively accounted for the time evolution of the PSD by resorting to the use of general population balance equations. This approach is fruitful in treating different particle growth processes as well. Actually, a formal description of crystallization along these lines has been developed some years ago by Hulburt and Katz.[16] However, the solution of the constitutive integrodifferential equations requires numerical techniques.[13,17,18] Among these kinds of approaches the most general and extensive model has been proposed by Min and Ray.[19] It stems from a set of complex, multivariate population balance equations coupled to energy and material balances for the reactor. However, the complexity of the model itself prevents practical applications mainly because it requires the knowledge of a large set of parameters that very often are not experimentally available.

The other approach that has evolved strives to provide analytic solutions to the prediction of the time evolution of the PSD. For batch polymerizations in the SE Interval II, solutions were given by O'Toole,[20] Watterson and Parts,[21] Lichti and co-workers,[22,23] and more recently Feeney[24] and Chen.[25] The starting point for all these theoretical interpretations rests on a closed solution of the population balance equations that describes the time evolution of the PSD. However, owing to the complexity of the problem, up to now analytic solutions have been achieved only for the so-called zero–one system.

In this paper we will provide a general, comprehensive method for the analytic solution of the population balance equations for the SE Interval II. In our approach the

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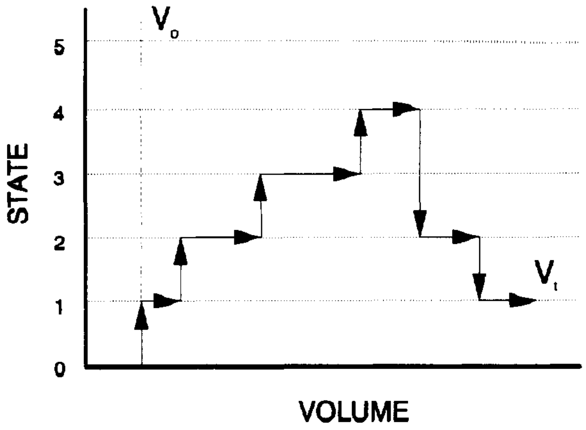

Figure 1. Phase diagram of the possible states. The trajectory represents the growth history of a single latex particle, i and V_t corresponding to number of radicals in the particle and its volume at reaction time t. V_0 is the volume at $t = 0$.

restriction connected to the "instantaneous termination" hypothesis can be easily lifted, making allowance also for bimolecular termination reactions. The core of this proposed method is a particular combination of transforms that allows a PSD-generating function to be constructed. For any particular case under scrutiny the analytic form of this generating function can be found by solving an associated partial differential "wave equation". All the information connected to the time evolution of the PSD is encapsulated in this function and hence the term "wave equation".

Theoretical Framework. An emulsion polymerizing system is considered where the overall number of reaction loci does not vary with time; i.e., we consider a seeded polymerization or a system that already entered the SE Interval II.

To specify the PSD of the growing latex, it is necessary to define two distinct number density distributions. Actually, latex particles can be classified according to either the number of the growing radicals they contain or their volume. As already pointed out,[9] the overall process of latex growth may be grasped more clearly by means of the simple energy level diagram shown in Figure 1. If a certain latex particle contains i radicals and has a volume v at time t, we shall say that this particle at that moment is in a specific state (i,v) represented by a point on the "energy level diagram". Over the course of time the elementary reactions involved in the process cause a given particle to change its state by entry of a new radical, by exit (and/or monomolecular termination), and by mutual annihilation between two growing radicals as well as by an increase in its volume due to the conversion of the monomer into polymer. The total evolution of states of any latex particle in time is uniquely described by a trajectory of the point on the phase plane (see Figure 1). To describe the state of a latex containing a large number of particles, first, we define as $N_i(t)$ the number fraction distribution of the latex particles with respect to radical occupancy i at any reaction time t. Furthermore, since reaction loci must be classified also according to their size v, we define as $n_i(v,t)$ the number density distribution of particles of volume v in state i at time t. This last distribution is related to $N_i(t)$ through

$$N_i(t) = \int_0^\infty n_i(v,t)\,\mathrm{d}v \qquad (1)$$

The actual PSD $\mathbf{n}(v,t)$ at any reaction time t may be calculated by summation over all states:

$$\mathbf{n}(v,t) = \sum_{i=0}^{\infty} n_i(v,t) \qquad (2)$$

According to Lichti et al.[22] for the particular system under consideration, the particle growth can be described by the set of population balance equations

$$\frac{\partial n_i(v,t)}{\partial t} = \rho(n_{i-1} - n_i) + k[(i+1)n_{i+1} - in_i] + c[(i+2)(i+1)n_{i+2} - i(i-1)n_i] - \frac{\partial}{\partial v}(K_{ii}n_i) \qquad (3)$$

where ρ, k, and c are, respectively, the pseudo-first-order rate constants for entry, exit, and bimolecular termination.

In eq 3 K_{ii} denotes the volume growth rate of a particle containing i free radicals. One common assumption regarding K_{ii} is that

$$K_{ii} = iK \qquad (4a)$$

$$K = 10^{21}k_\mathrm{p}C_\mathrm{M}M_0/(N_\mathrm{A}d_\mathrm{p}) \qquad (4b)$$

In the last equation for the factor 10^{21} is required for making the two sides have the same dimension, K (nm^3 s^{-1}) is the volume growth rate of a particle containing one free radical, k_p (dm^3 mol^{-1} s^{-1}) the propagation rate constant, C_M (mol dm^{-3}) the monomer concentration in the particles, M_0 (g mol^{-1}) the molecular weight of the monomer, N_A (mol^{-1}) Avogadro's number, and d_p (g cm^{-3}) the density of the amorphous polymer. We note here that eq 4a holds true only if particle growth is not limited by monomer diffusion or if monomer concentration does not depend on particle size.[26] The pseudo-first-order rate coefficients for radical entry, radical exit, and bimolecular termination have been shown to be dependent upon both the state[27] and the volume of the latex particles.[28] However, in the following treatment we shall assume that all the rate coefficients remain constant. This assumption seems justified whenever the time interval is not too long or the variation in volume of the particles is not too large.

Under the above-mentioned restrictions, eq 3 constitutes an infinite set of linear partial differential difference equations. The mathematical handling of these kinds of equations can be highly simplified by applying suitable transforms. In the particular case the evolution of the system can be described in terms of three different variables: the reaction time, t, the number, i, of growing radicals inside each latex particle, and the actual particle size, v. However, when reaction time is the independent variable, suitable transforms need to be worked out only for the "state" and the size of the reaction loci.

The number i of growing radicals is a discrete unit whereas the particle size grows continuously. Accordingly, a continuous transform has to be applied with respect to the particle size, while a discrete one needs to be found for the description of the associated growing radicals. We begin by taking a Laplace transform of $n_i(v,t)$ with respect to v

$$\mathcal{L}_i(s,t) = \int_0^\infty \exp(-sv)\, n_i(v,t)\,\mathrm{d}v \qquad (5)$$

where the subscript i refers to the state of the particle and s is the Laplace variable conjugate to volume v. Since $n_i(0,t) = 0$, eq 3 can be rewritten in terms of the integral transform 5

$$\frac{d\mathcal{L}_i}{dt} = \rho[\mathcal{L}_{i-1} - \mathcal{L}_i] + k[(i+1)\mathcal{L}_{i+1} - i\mathcal{L}_i] + c[(i+2)(i+1)\mathcal{L}_{i+2} - i(i-1)\mathcal{L}_i] - sKi\mathcal{L}_i \quad (6)$$

As a second step, we introduce the generating function for the Laplace transforms $\mathcal{L}_i(s,t)$

$$\Psi(x,s,t) = \sum_{i=0}^{\infty} \mathcal{L}_i(s,t)x^i \quad (7)$$

The following properties of $\Psi(x,s,t)$ are immediately obvious from its definition:

(i) For $s = 0$ it must reduce itself to the generating function for the fractional locus populations $N_i(t)$.[29]

(ii) At the point $x = 1$ the function $\Psi(1,s,t)$ corresponds to the Laplace transform of the volume probability density function (pdf) of latex particles at reaction time t.

(iii) Owing to the properties of the Laplace transform,[30] the rth moment about the origin of the volume pdf is given by

$$\mu_r(t) = (-1)^r \left(\frac{\partial^r \Psi}{\partial s^r}\right)_{x=1;s=0} \quad (8)$$

(iv) The Laplace transform of the volume pdf of particles in state i is

$$\mathcal{L}[n_i(v,t)] = \frac{1}{i!}\left(\frac{\partial^i \Psi}{\partial x^i}\right)_{x=1} \quad (9)$$

To be acceptable, the generating function must be infinitely derivable with respect to x and s and its derivatives must be finite at the points $s,x = 0$ and $x = 1$. This follows because physically these quantities represent the sum of products of the number of loci and numbers of radicals or the moments about the origin relative to the volume pdf of some distinctive latex particles.

Boundary conditions of the Ψ function deserve particular attention. In this treatment we are dealing only with seeded polymerizations or with systems that already entered the SE Interval II. Moreover, the $\Psi(x,s,t)$ generating function is related somehow to the Laplace transform of the actual PSD. Accordingly, it turns out that at reaction time $t = 0$ it must be

$$\Psi(1,s,0) = \mathcal{L}[\mathbf{n}(v,0)] \equiv \mathcal{L}^{\circ}(s) \quad (10)$$

where $\mathcal{L}^{\circ}(s)$ is the Laplace transform of the PSD of the seed or of the reacting latex at conventional time $t = 0$.

Once the analytic form of the generating function is known, the time evolution of the PSD is given by

$$\mathbf{n}(v,t) = \mathcal{L}^{-1}[\Psi(1,s,t)] \quad (11)$$

where $\mathcal{L}^{-1}[\ ]$ is the inverse Laplace transform. Unfortunately analytic Laplace transform inversion is not always an easy task to accomplish or, in the worst cases, it is not possible at all. From the other side, however, many experimentally determinable quantities are related not to whole PSD but only to some distinctive moments or to a particular combination of moments. To this end, some useful mathematical devices have been introduced, namely the characteristic function (CF) and the cumulant generating function (CGF).[31] The generating function $\Psi(x,s,t)$ is related in a simple fashion to both of them. Actually the CF of the PSD is defined as

$$\Phi(\tau,t) = \int_0^{\infty} \exp(j\tau v)\, \mathbf{n}(v,t)\, d\tau; \quad j = (-1)^{1/2} \quad (12)$$

As is well-known, the relationship between the CF and the rth moment about the origin is

$$\left[\frac{d^r}{d\tau^r}\Phi(\tau)\right]_{\tau=0} = j^r \mu_r \quad (13)$$

If we compare eqs 8 and 13, it can be easily proven that $\Psi(1,s,t)$ converges to the CF through the substitution

$$s = -j\tau \quad (14)$$

Of more interest is the CGF defined as[30]

$$\ln \Phi(\tau,t) = \sum_{r=1}^{\infty} k_r(t)\frac{(j\tau)^r}{r!} \quad (15)$$

where $k_r(t)$s are the cumulants or the semiinvariants of the PSD. The first few semiinvariants are

$$k_1 = \mu_1^* = m \quad (16a)$$

$$k_2 = \mu_2^* = \sigma^2 \quad (16b)$$

$$k_3 = \mu_3^* \quad (16c)$$

$$k_4 = \mu_4^* - 3(\mu_3^*)^2 \quad (16d)$$

where m is the mean, σ^2 the variance, and μ_r^* the rth central moment of the PSD. The 3rd and 4th cumulants are related, respectively, to the skewness, γ_1, and the excess or kurtosis, γ_2, of the latex PSD.

$$\gamma_1 = k_3/(k_2)^{3/2} = \mu_3^*/\sigma^3 \quad (17a)$$

$$\gamma_2 = k_4/(k_2)^2 = \mu_4^*/\sigma^4 - 3 \quad (17b)$$

Also in this case, from the definition and the properties of the generating function $\Psi(x,s,t)$, it can be shown that

$$k_r(t) = (-1)^r\left[\frac{\partial^r \ln \Psi}{\partial s^r}\right]_{x=1;s=0} \quad (18)$$

Solutions to the Generating Function. To convert the infinite set of differential difference equations 6 into a single differential equation in Ψ, each equation for $d\mathcal{L}_i/dt$ is multiplied by x^i, and then all the equations so obtained are summed. By our making use of standard relationships[29] involved in the power transform 7, the following "wave equation" results:

$$\frac{\partial \Psi}{\partial t} = \rho(x-1)\Psi + k(1-x)\frac{\partial \Psi}{\partial x} + c(1-x^2)\frac{\partial^2 \Psi}{\partial x^2} - sKx\frac{\partial \Psi}{\partial x} \quad (19)$$

Formally, this equation does not differ very much from the generating equation for the fractional locus population, $N_i(t)$.[29] Apparently the only difference is due to the last term on the right-hand side containing the volume growth rate, K. However, contrary to the Stockmayer–O'Toole treatment, eq 19 does not allow steady-state solutions because it describes only the PSD time evolution. Accordingly, one has to deal only with partial differential equations. Although entirely general solutions to eq 19 have been elusive, we succeeded in obtaining general solutions to a modified set of equations that, under certain circumstances, approximate the exact equation. We begin with the simplest case first.

Solution for the Case Where $c = 0$. The problem is to solve the general "wave equation", setting $c = 0$.

$$\frac{\partial \Psi}{\partial t} = \rho(x-1)\Psi + k(1-x)\frac{\partial \Psi}{\partial x} - sKx\frac{\partial \Psi}{\partial x} \quad (20)$$

We consider first a seeded system in which, at reaction time $t = 0$, all the latex particles are in state 0 (i.e., $N_0(0) = 1$). In this case (see Appendix A) the solution of eq 20

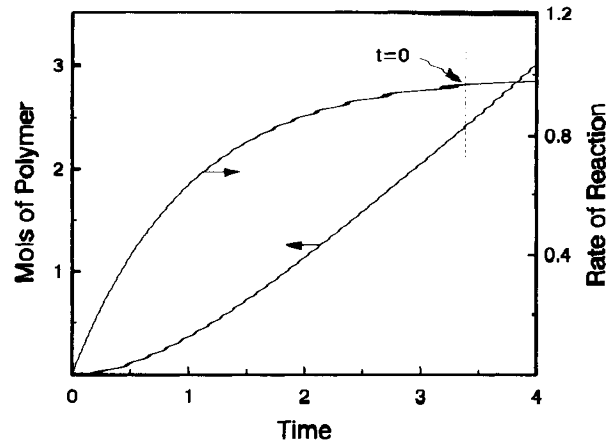

Figure 2. Boundary conditions for an emulsion reacting system with a steady-state $N_i(t)$ free-radical distribution: the arrow indicates the conventional time $t = 0$.

is readily found to be

$$\Psi(x,s,t) = \mathcal{L}^\circ(s) \exp\{(\rho/A^2)[k - Ax](\exp[-At] - 1) + (k/A - 1)\rho t\}; \quad A = k + sK \quad (21)$$

Since, by definition

$$\int_0^\infty \mathbf{n}(v,0)\, dv = 1$$

at the point $x = 0$ we obtain

$$\Psi(x,0,t) = \exp\left\{\frac{\rho}{k}(x - 1)[1 - \exp(-kt)]\right\} \quad (22)$$

which is exactly the generating function for the $N_i(t)$ distribution of a seeded system where $N_0(0) = 1$.[29]

It is worth taking into account also another boundary condition, i.e., a reacting system where the $N_i(t)$ distribution has already reached its stationary state. This condition represents a case of practical interest when dealing with ab initio emulsion reactions. Once the system enters the SE Interval II and the reaction rate reaches its steady-state value, the PSD at time t^* may be taken as $\mathbf{n}(v,0)$ through a simple time-scale shift (Figure 2). The value of $\mathbf{n}(v,0)$ as well as the PSD time evolution can be determined experimentally by sampling the reacting system at progressive time intervals.[28] Given this boundary condition, the following solution to eq 20 results (see Appendix A)

$$\Psi(x,s,t) = \mathcal{L}^\circ(s) \exp\left[\rho\left(\frac{k}{k + sK} - 1\right)t + \frac{\rho}{k + sK}(x - 1)\right] \quad (23)$$

Again, we note that at the point $s = 0$ eq 23 converges to the generating function for the $N_i(\infty)$ distribution[29]

$$\Psi(x,0,\infty) = \exp[(\rho/k)(x - 1)] \quad (24)$$

As previously pointed out, for $x = 1$ the Ψ function is directly related to the CF of the PSD. Both eqs 21 and 23 are made up of the product of two distinct functions, the time-independent $\mathcal{L}^\circ(s)$ function and a time-dependent one. According to the properties of the characteristic function,[31] this means that the PSD time evolution is independent of the initial latex PSD. This is clarified further by taking into account the CGF. For the reacting system described by the generating function 21, the related CGF is

$$\vartheta(s,t) = \vartheta^\circ(s) + \frac{\rho}{(k + sK)^2}[k - (k + sK)x]\}\exp[-(k + sK)t] - 1\} + \left[\frac{k}{k + sK} - \rho\right]t \quad (25)$$

where $\vartheta^\circ(s) = \ln \mathcal{L}^\circ(s)$ is the CGF of the $\mathbf{n}(v,0)$ PSD. From eq 18 it is possible to elaborate the following general formula for the rth cumulant of the PSD at reaction time t

$$k_r(t) = k_r(0) + \bar{n}_{ss} r! \frac{1}{\beta^r}\left\{\exp(-kt)\sum_{m=0}^{r}\frac{(r - m)}{m!}(kt)^m - r\right\} + \frac{r!}{\beta^r}\rho t; \quad r > 0 \quad (26)$$

where $\bar{n}_{ss} = \rho/k$ is the steady-state value of the average number of radicals per particle and $\beta = k/K$.

For an emulsion polymerization whose latex particles already reached the steady-state distributions $N_i(\infty)$ the CGF is

$$\vartheta(s,t) = \vartheta^\circ(s) - \frac{\rho s t}{s + \beta} \quad (27)$$

In this case the rth cumulant has the following simplified expression:

$$k_r(t) = k_r(0) + (r!/\beta^r)\rho t \quad (28)$$

From eqs 26 and 28 it can be easily seen that over the long term the cumulants of the PSD are linearly dependent on time both in the transient and nontransient cases.

Approximate Solutions for the Case Where $c > 0$. For a reacting system where second-order processes are not of negligible occurrence with respect to both zero- and first-order elementary events, the generating function $\Psi(x,s,t)$ can be found by solving the related partial differential "wave equation" 19. We note here that at the point $s = 0$ we are dealing with the time-dependent SE differential difference equations in their most general form.[29] Although considerable effort has been devoted in recent years to the problem of finding explicit analytic solutions to this set of equations,[32-34] it has so far been necessary to resort to approximation procedures.

Britwistle and Blackley[35] obtained an interesting general solution for transient conditions. In their approximate treatment, the factor $1 - x^2$ in the third term of the right-hand side of eq 19 was replaced by $1 - x$ with justification from both mathematical and physical arguments. More recently Song and Poehlein[36] discussed the approximate "Poisson" solution given by Blackley. They showed that since $(1 - x^2) = (1 - x)(1 + x)$, Blackley improperly assumed that $1 + x$ can be approximated by 1 instead of 2. This factor of 2 results from the bimolecular termination of radicals. In the present case, it is also a direct consequence of the fact that, for our purposes, it is the behavior of $\Psi(x,s,t)$ around the point $x = 1$ that is of interest. Accordingly, provided that the *dominant radical-loss mechanism is not second order*, eq 19 can be safely replaced by

$$\frac{\partial\Psi}{\partial t} = \rho(x - 1)\Psi + k(1 - x)\frac{\partial\Psi}{\partial x} + 2c(1 - x)\frac{\partial^2\Psi}{\partial x^2} - sKx\frac{\partial\Psi}{\partial x} \quad (29)$$

Equation 29 can be solved in terms of Kummerer's confluent hypergeometric functions.[37] For a seeded system, where, at reaction time $t = 0$, $N_0(0) = 1$, a complex expression results (see Appendix B). However, after algebraic manipulation, for $s = 0$ the generating function reduces to the approximate Poisson solution found by Blackley[35] for the $N_i(t)$ generating function

$$\Psi(x,0,t) = \exp[\theta(t)(x-1)] \qquad (30a)$$

$$\theta(t) = \frac{2\rho \tanh(ht/2)}{h + \tanh(ht/2)}; \quad h = (8\rho c + k^2)^{1/2} \qquad (30b)$$

Also in this case a simpler expression of Ψ results for the case of a reacting system that at time $t = 0$ has already reached its stationary-state distribution for the fractional locus population $N_i(t)$ (Appendix B)

$$\Psi(x,s,t) = \mathcal{L}^\circ(s) \exp\left\{\frac{2\rho}{D + (k + sK)}[(x-1) - sKt]\right\} \qquad (31)$$

where $D^2 = (k + sK)^2 + 8\rho c$. Again, for $x = 0$, eq 31 gives the generating function for the $N_i(\infty)$ locus population distribution arising from the approximation introduced by Blackley.[35]

$$\Psi(x,0,t) = \exp\left\{\frac{2\rho}{h+k}(x-1)\right\} \qquad (32)$$

Please note that in the limit $c = 0$ eq 32 correctly reduces to eq 24. Moreover, the CGF can be expressed by the simple equation

$$\vartheta(s,t) = \vartheta^\circ(s) - \frac{2\rho sKt}{D + (k + sK)} \qquad (33)$$

Also in this case the rth cumulant of the PSD is linearly dependent on time. Actually from eq 33 it is possible to derive the following general equation:

$$k_r(t) = k_r(0) + \frac{r!}{(\beta^2 + a^2)^{1/2} + \beta}\,\frac{2\rho t}{[(\beta^2 + a^2)^{1/2}]^{r-1}}; \quad a^2 = (8\rho c)/K^2 \qquad (34)$$

Again in the limit $c = 0$ eq 34 leads to eq 28.

Time Evolution of the PSDs. In this section we will take into account only systems whose radical occupancy has already reached the stationary-state distribution. Analytic expressions of the related moment generating function Ψ are comparatively simpler than those describing systems where the boundary condition is $N_0(0) = 0$. Basically, the problem of finding the $\mathbf{n}(v,t)$ PSD from the generating function Ψ relates to the more general problem of analytic integral transform inversion. A number of different techniques are available. In the present case the Ψ function is the generating function of the Laplace transforms of the $n_i(v,t)$ distributions. Accordingly the problem becomes one of inverse Laplace transform. As usual we begin by taking into account the simplest case, i.e., an emulsion reacting system where $c = 0$. From eqs 11 and 23 we have

$$\mathbf{n}(v,t) = \mathcal{L}^{-1}\left[\exp(-\rho t)\mathcal{L}^\circ(s)\exp\left(\frac{\rho\beta t}{s+\beta}\right)\right] \qquad (35)$$

The problem of the inversion of eq 35 can be tackled in different ways. We prefer, first, to multiply both sides by $\exp(\rho t)$ and then to take the derivative with respect to time.

$$\frac{\partial}{\partial t}\{[\exp(\rho t)\,\mathbf{n}(v,t)]\} = \mathcal{L}^\circ(s)\frac{\rho\beta}{s+\beta}\exp\left\{\frac{\rho\beta t}{s+\beta}\right\} \qquad (36)$$

By taking the inverse Laplace transform of eq 36 and integrating both sides with respect to time, we have

$$\mathbf{n}(v,t) = \{\beta\int_0^{x=t}[\int_0^v \mathbf{n}(v-\tau,0)\exp(-\beta\tau) \times I_0[2(\rho\beta t\tau)^{1/2}]\,\mathrm{d}\tau]\,\mathrm{d}x + n(v,0)\}\exp(-\rho t) \qquad (37)$$

Reversing the order of integration and then integrating finally gives

$$\mathbf{n}(v,t) = \exp(-\rho t)\left\{\mathbf{n}(v,0) + \int_0^v \mathbf{n}(v-\tau,0)\exp(-\beta\tau)\left(\frac{\rho\beta t}{\tau}\right)^{1/2} I_1[2(\rho\beta t\tau)^{1/2}]\,\mathrm{d}\tau\right\} \qquad (38)$$

Three main results are immediately obvious:

(i) The PSD relaxes with time according to a simple exponential law whose characteristic time is $1/\rho$.

(ii) The time evolution of the PSD is made up of two distinct parts. The first represents the memory of the PSD at $t = 0$. The second is given by a convolution integral between the initial PSD and an expression containing a modified Bessel function of order 1.

(iii) The time evolution of the PSD *depends only on two parameters* (ρ and $\beta = k/K$).

Despite its complexity, once $\mathbf{n}(v,0)$ has been specified, eq 38 can be evaluated numerically with trivial computational time by using simple Gaussian quadrature. For the case of $\mathbf{n}(v,0) = \delta(v-V)$, where $\delta(v-V)$ is the delta Dirac function, the PSD time evolution is accounted for by a comparatively simpler expression, where convolution integrals are not involved.

$$n(v,t) = \left\{\delta(v-V) + \exp[-\beta(v-V)]\left(\frac{\rho\beta t}{v-V}\right)^{1/2} I_1[2(\rho\beta t)^{1/2}(v-V)^{1/2}]\,\mathcal{U}(v-V)\right\}\exp(-\rho t) \qquad (39)$$

In eq 39 $\mathcal{U}(v-V)$ represents the Heaviside unity step function. It is worth noting that in the limit $v = V$ eq 39 takes the following expression:

$$\lim_{v\to V}\mathbf{n}(v,t) = \{\delta(v-V) + \exp(-\beta V)\rho\beta t\}\exp(-\rho t) \qquad (40)$$

Finally, according to eq 9, it is possible to find also simple expressions for the contribution to the overall PSD at a given time t of latex particles containing a number i of growing radicals. Actually we have

$$\mathcal{L}[n_i(v,t)] = \mathcal{L}^\circ(s)\frac{(\rho^*)^i}{i!}\frac{1}{(s+\beta)^i}\exp\left(\frac{\beta t - \rho^*}{s+\beta}\right) \qquad (41)$$

where $\rho^* = \rho/K$. By standard inversion techniques we have

$$n_i(v,t) = \frac{(\rho^*)^i}{i!}\exp(-\rho t)\int_0^v \mathbf{n}(v-\tau,0)\exp(-\beta\tau) \times \left(\frac{\tau}{\beta t - \rho^*}\right)^{(i-1)/2} Z_{i-1}\{2[(\rho\beta t - \rho^*)\tau]^{1/2}\}\,\mathrm{d}\tau \qquad (42)$$

where

$$Zn(X) \longrightarrow \begin{cases} In(X); & t > 1/k \\ Jn(X); & t < 1/k \end{cases} \qquad (43)$$

In the particular case of $t = 1/k$ eq 42 reduces to

$$n_i(v,t) = \frac{(\rho^*)^i}{i!}\frac{1}{(i-1)!}\exp(-\rho t)\int_0^v \mathbf{n}(v-\tau,t)\tau^{i-1} \times \exp(-\beta\tau)\,\mathrm{d}\tau; \quad i > 0 \qquad (44)$$

It is worth noting that, owing to the properties of the Laplace transform

$$N_i(t) = \int_0^\infty n_i(v,t)\,\mathrm{d}v = 1/i!(\rho/k)^i \exp(-\rho/k) \times \lim_{s\to 0} \mathcal{L}[\mathbf{n}(v,t)] \quad (45)$$

As can be easily verified

$$\lim_{s\to 0} \mathcal{L}[\mathbf{n}(v,t)] = 1 \quad (46)$$

This follows because of the normalization condition of the PSD. Accordingly, eq 46 gives exactly the same results of the Blackley treatment.[35]

For the case of reacting systems where $c > 0$ from eqs 11 and 31 we have

$$\mathbf{n}(v,t) = \mathcal{L}^{-1}\left\{\mathcal{L}^\circ(s) \exp\left[\frac{-2\rho t s}{[(s+\beta)^2 + a^2]^{1/2} + (s+\beta)}\right]\right\} \quad (47)$$

where $a^2 = 8\rho^* c^*$ and $c^* = c/K$. Although it is not possible to find simple expressions for the inversion of eq 47, some useful series summation formulas can still be obtained. In Appendix C full details are given for the inversion procedures. The first inversion formula obtained is

$$\mathbf{n}(v,t) = \mathbf{n}(v,0) - Kt(\rho/2c)^{1/2}\sum_{n=0}^{\infty}(-1)^n\frac{1}{n!}[(\rho/2c)^{1/2}Kt]^n\zeta_n \quad (48)$$

where

$$\zeta_n = \int_0^v \mathbf{n}(v-\tau,0)\frac{\mathrm{d}^n}{\mathrm{d}\tau^n}\left\{\exp(-\beta\tau)\frac{1}{\tau}J_{n+1}(a\tau)\right\}\mathrm{d}\tau \quad (49)$$

It is worth noting that $(\rho/2c)^{1/2} = \bar{n}_{\mathrm{bulk}}$ is the average number of radicals per latex particle, assuming no compartimentalization effect. Another interesting result comes out by taking the derivative of eq 47, first, with respect to c and, then, integrating the resulting expression.

$$\mathbf{n}(v,t) = \mathbf{n}(v,t)|_{c=0} - \sum_{n=0}^{\infty}(-2\rho t)^{n+1}\frac{1}{n!}\int_0^v \mathbf{n}(v-\tau,0)\frac{\mathrm{d}^{n+1}}{\mathrm{d}\tau^{n+1}} \times \left\{\left[\frac{\tau^n}{2^{n+1}}\frac{1}{(n+1)!} - 1/(a\tau)^{n+1}J_{n+1}(a\tau)\right]\exp(-\beta\tau)\right\}\mathrm{d}\tau \quad (50)$$

In eq 50 the PSD $\mathbf{n}(v,t)$ values are given as perturbations of the time evolution of a corresponding system where $c = 0$ (see eq 38).

Results and Discussion

Theoretical Predictions. Figures 3–5 show some typical results from calculations of the time evolution of PSDs for reacting systems where $c = 0$. The plots are in dimensionless variables and were obtained by selecting representative values for the parameters.

Figure 3 corresponds to a seeded reaction (eq 38) where the initial PSD can be satisfactorily represented by the Γ distribution.

$$\mathbf{n}(v,0) = \frac{b^\alpha}{\Gamma(\alpha)}v^{\alpha-1}\exp(-bv); \quad \alpha,b > 0 \quad (51)$$

In this simulation we set $\rho = K = 1$ and $k = 10$. Here the coupling from the growing to the nongrowing states, namely N_0, is very strong so that at any time most of the particles are nongrowing. As a result, $\bar{n}_{\mathrm{ss}}$ is much lower than 0.5. This situation corresponds to reacting systems where exit reactions are overwhelming, like for example vinyl acetate polymerization. It is worth noting that, although in the present approach bimolecular chain-stopping events are neglected (i.e., we assume $c \ll \rho, k$), this method can be easily extended also to systems conforming to the well-known zero–one system, i.e., a system where $c \gg \rho, k$. To this end we need only to substitute the exit rate constant k by a new pseudo-exit rate constant ($k + 2\rho$). There are different justifications[5,36] for this substitution.

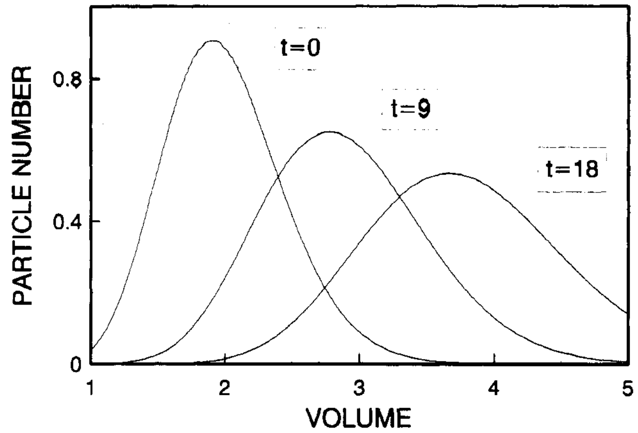

Figure 3. Theoretical PSDs as a function of volume (dimensionless units) obtained by eq 38. Parameters: $\rho = k = 1$; $K = 10$. PSD at $t = 0$ is a Γ distribution.

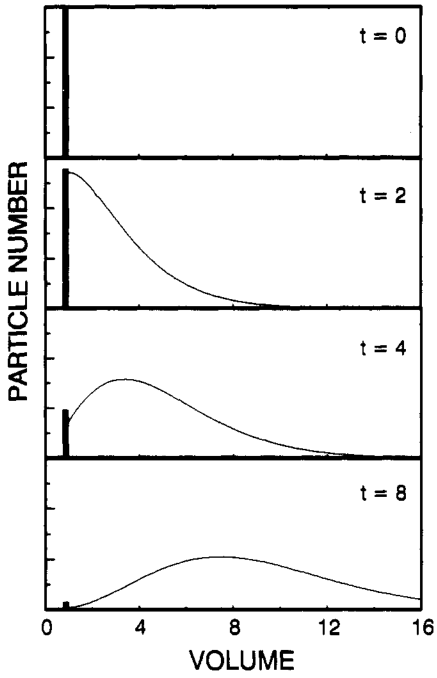

Figure 4. Theoretical PSDs as a function of volume (dimensionless units) obtained by eq 39. Parameters: $\rho = k = K = 1$. PSD at $t = 0$ is a δ Dirac function.

Figure 4 shows the case of a system where the initial particle size distribution is monodispersed and $\rho = k = K = 1$. The equality of the entry and the exit rate constants means that the average number of growing radicals, $\bar{n}_{\mathrm{ss}} = \rho/k = 1$, is 10 times larger than that in the previous case.

Finally in Figure 5 we report at a given reaction time the PSD of a seeded system where $\rho = k = 1$ and $K = 0.5$. Data are evaluated through eqs 38 and 42, and the initial PSD is assumed to be the Γ distribution. Also reported are the contributions to the overall PSD of latex particles having 0–3 growing radicals, respectively.

All the convolution integrals involved in these examples were evaluated by Gaussian quadrature: calculations were

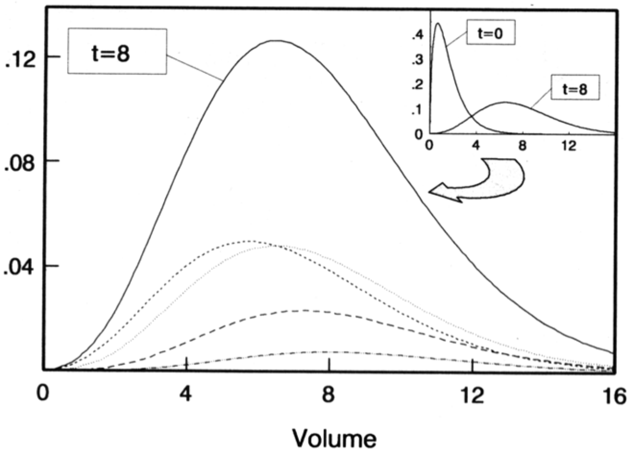

Figure 5. Theoretical PSDs as a function of volume (dimensionless units) obtained by eqs 38 and 42: (—) $n(v,t)$; (- - -) $n_0(v,t)$; (· · ·) $n_1(v,t)$; (– –) $n_2(v,t)$; (– · · –) $n_3(v,t)$. Parameters: $\rho = k = 1$, $K = 0.5$. PSD at $t = 0$ is a Γ distribution.

made on a personal computer with negligible computational effort.

The effect of the entry and exit rate coefficients on the polydispersity of the resulting latex has been already discussed with reference to the zero–one system.[24] The key parameter in controlling the polydispersity of a latex is the entry rate of free radicals. The same conclusion can be drawn from eq 28 in a straightforward way. One of the outstanding advantages of our approach over those previously reported is the ability to theoretically predict also the effect on polydispersity of bimolecular versus monomolecular termination reactions. To this end, it is worth considering two growing latexes in the nontransient state. Both these systems have the same entry rate and the same average number of radicals per latex particle, $\bar{n}_{ss}$. However, in the first polymer chains are formed only by monomolecular termination reactions, whereas in the second bimolecular termination is also operative. Given the above constraints (same $\bar{n}_{ss}$ and ρ), in the system where bimolecular reactions are allowed the monomolecular termination constant k^* must be

$$k^* = k - (2\rho c)/k \tag{52}$$

This result comes out by applying the "Poissonian" approximation of Blackley for the evaluation of $\bar{n}_{ss}$. Obviously c is always $\leqslant k^2/2\rho$. By substitution of eq 52 into eq 35 it is possible to draw analytical conclusions on the effect of polydispersity of bimolecular vs monomolecular termination. The results obtained are reported in Figure 6 at increasing values of c/k. For the sake of simplicity we consider a seeded reaction where the seed is a monodispersed latex of volume $v = 1$ and $\rho,k = K = 1$. As can be easily seen the coefficient of variation $CV = \sigma/m$ is inversely related to c/k. The physical reason for c playing such a pivotal role in determining the polydispersity of latex particles is the same as that already invoked for ρ.[24] Actually, since polydispersity is a consequence of different growth regimes in different particles, the higher the ratio between the rate of bimolecular vs monomolecular termination, the lower the difference of the growth rate between latex particles. This leveling effect of bimolecular termination reactions is due to the mutual annihilation of two growing radicals whereas only one polymer chain ceases to grow by monomolecular termination reactions.

Comparison with Previously Reported Treatments. Integral transform techniques have already been used by different authors[23-25] for the description of the time evolution of PSDs. Only the zero–one system was taken into account. Moreover, it must be clearly pointed out that in all these treatments integral transforms were used just for a *mechanical* solution of a system of two partial differential equations.

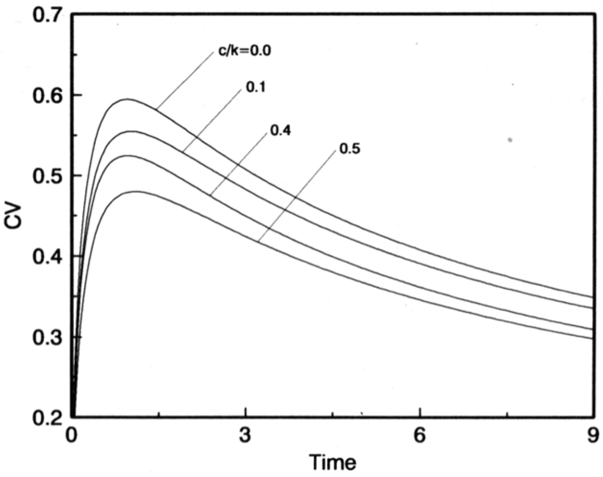

Figure 6. Theoretically predicted coefficient of variation (CV) of the volume as a function of time (dimensionless units) and for systems having the same $\bar{n}_{ss}$ and ρ but different c/k (eqs 32 and 52).

Lichti[23] and Feeney[12] extensively used the complex Fourier transform, solving then the resulting differential equations by the eigenvalue method. The function $\mathbf{n}(v,t)$ was finally given in terms of the general Fourier inversion formulas. However, this method involves numerical evaluations of exponential integrals in the complex plane. The same authors also took the Laplace transform with respect to time and solved the zero–one system for $\mathbf{n}(v,0)$, conforming to a monodispersed PSD. Solutions were given in terms of modified Bessel functions, although no simple and general equations were presented.

In discussing the kinetic factors that determine the polydispersity of polystyrene latices, Feeney[24] introduced the moment equation by resorting to a Mellin type transform. Analytic expressions were given for the first and the second moments. They are equivalent to the more general eq 26 given in this paper. No analytic expression was reported for the higher moments, because the mathematical handling of the moment equations becomes extremely cumbersome after the first two moments. The main reason for this is due to the Mellin transform of the growth term $K\partial n_i/\partial v$ in the SE equations, which leads to a set of coupled "closed" ordinary differential equations.[38]

Recently Chen and Wu[25] used the Laplace transform for the solution of the PSD time evolution of a zero–one seeded system. These authors gave equations for the first three cumulants. These expressions, however, differ from those reported in this paper. The time evolution of the first three cumulants was given by Wu and Chen only in terms of the kinetic constants ρ, k, and K. The lack of any memory of the initial seed was justified, speculating that "the time t... is not the reaction time. It merely represents the time t' at which PSD has the values μ_1, μ_2, and μ_3." In our opinion, although the Laplace transform was applied correctly, initial boundary conditions were questionable. Actually, they were taken implicitly by normalization at the point $s = 0$. After the reduction of the set of the two partial SE differential equations to ordinary equations, the Laplace conjugate variable s no longer behaves as a true variable. It should be considered as a *parameter*. On the contrary, if the boundary conditions (given by the Laplace transform of $\mathbf{n}(v,0)$) are

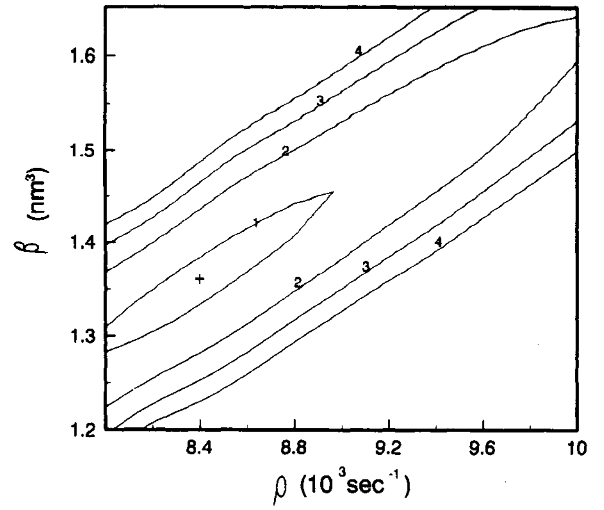

Figure 7. Counterplot diagram of the surface of residuals f (eq 53) for the styrene PSD at a 35-min fitting (data from ref 28): curve 1, 3×10^{-5}; curve 2, 6×10^{-5}; curve 3, 9×10^{-5}; curve 4, 1.2×10^{-4}.

set with respect to time $t = 0$, results compatible with those of the preceding sections can still be achieved. However, it must borne in mind that, starting from the zero-one system, it would be impossible to achieve a generalization of the description of PSDs as that presented in this paper.

Comparison with Experimental Data. When theoretical predictions are compared with experimental data, a common practice is to resort to model systems. For free-radical polymerizations (both homogeneous and heterogeneous) the model of choice is styrene. As clearly demonstrated by an impressive body of data,[1] the emulsion polymerization of styrene follows the zero-one kinetics if small particles are used. Accordingly, in applying the predictions of our theoretical approach, hereafter we shall make use of eqs 21–27 and 35–44, replacing the exit rate constant k by the new pseudo-exit constant $2\rho + k$.

Interest in analyzing the experimental time evolution of PSD is due mainly to the possibility of extracting the kinetic rate constants[23,38] as well as mechanistic information on their volume dependence.[28] This, however, requires very accurate experimental PSDs. In this connection, the data of Lichti[28] represent a benchmark against which the predictions of any theory should be tested. The experiment was an ab initio emulsion polymerization of styrene at 50 °C. The PSD data with unswollen volume v were measured at 20, 25, 30, and 35 min. Through this time interval, the rate of polymerization was constant within experimental error, so that it is reasonable to suppose that particle nucleation was complete. This allows eq 38 to be used. As a first step, from the observed PSDs successive pairs of $[\mathbf{n}(v,t),v]$ values were taken with an appropriate volume interval (60 experimental points were taken at least for each PSD determination). The first measured volume distribution, corresponding to $t = 20$ min, was taken as the initial PSD, $\mathbf{n}(v,0)$. This could be nicely fitted by the Γ distribution (eq 51). The α and b parameters were determined by a nonlinear least-squares (NLLS) fitting of experimental values. Next, setting this Γ distribution as the initial one, we tried to reproduce the experimental PSD at $t = 35$ min by using eq 38. The fitting involves finding the minimum, with respect to ρ and $\beta = (2\rho + k)/K$, of the function

$$f = \frac{1}{n}\sum_{n}[\mathbf{n}(v,t)_{\mathrm{exptl}} - \mathbf{n}(v,t)_{\mathrm{calc}}]^2 \qquad (53)$$

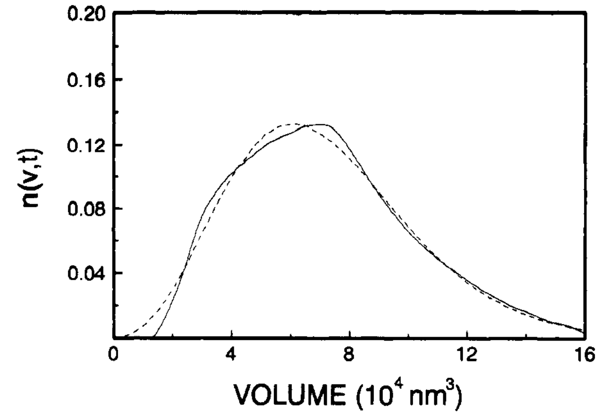

Figure 8. Comparison of theoretical PSD (eq 38) with experimental PSD at $t = 35$ min: (—) experimental data of Lichti et al.; (- - -) theory using $\rho = 8.4 \times 10^{-3}$ s^{-1}, $\beta = 1.36$ nm^3.

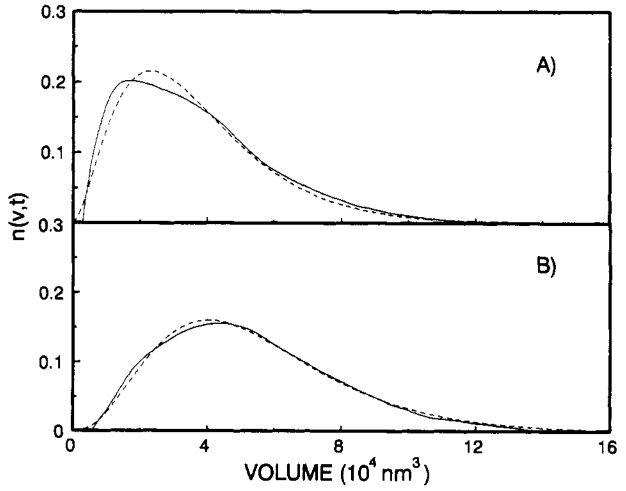

Figure 9. Comparison of theoretical PSDs with experimental PSDs at (A) $t = 25$ min and (B) $t = 30$ min: (—) experimental data of Lichti et al.; (- - -) theory, using $\rho = 8.4 \times 10^{-3}$ s^{-1}, $\beta = 1.36$ nm^3.

where the summation is over the n data points, $\mathbf{n}(v,t)_{\mathrm{calc}}$ is the fitted expression (calculated by eq 38), and $\mathbf{n}(v,t)_{\mathrm{exptl}}$ is the experimental value. The minimization is carried out using the SIMPLEX algorithm. The optimal values of the two parameters that determine the time evolution of the PSD are $\rho = 8.40 \times 10^{-3}$ s^{-1} and $\beta = 1.36$ nm^3. The sensitivity of the fitting of the data can be judged by examining the behavior of the residuals around the minimum value. This function is shown as a contour diagram in Figure 7. It is clearly apparent that the minimum of the surface representing eq 53 is fairly shallow; i.e., given the error propagation involved in the experimental determination of PSD,[23] there is a range of values that might provide a satisfactory fit to the data. It is also clear from Figure 8 that an excellent fit can be obtained with eq 38 and the optimized values of ρ and β. Furthermore, Figure 9 shows that fairly good agreement is obtained also at intermediate times.

A useful check on the validity of the methodology used to calculate the rate coefficients from PSD data is the agreement with the values, which can be determined directly from steady-state kinetics. Actually, from NLLS fitting of PSD one can obtain an estimate of both ρ and β or, alternatively, ρ and $K\bar{n}$. This last combination represents the growth rate of the mean of the PSD. This value can be extracted also from the fractional conversion

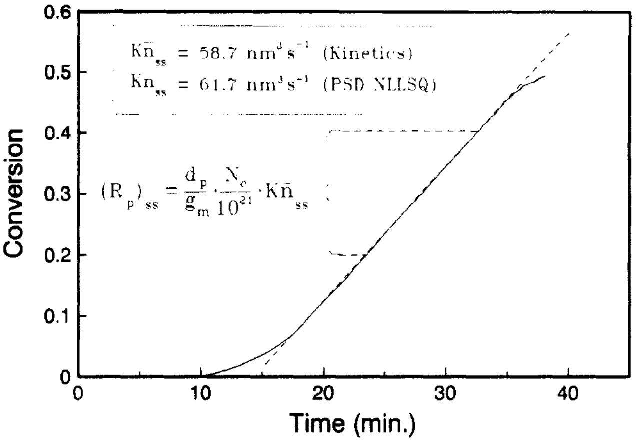

Figure 10. Mean growth rate, $K\bar{n}_{ss}$, of styrene polymerization calculated from experimental dilatometric data of fractional conversion vs time.[28]

vs time curve. Actually, at steady state, we have

$$K\bar{n}_{ss}\ (\mathrm{nm}^3\ \mathrm{s}^{-1}) = \frac{g_m}{d_p}\frac{10^{21}}{N_c}(R_p)_{ss} \tag{54}$$

where g_m (g dm^{-3}) is the initial mass of monomer per unit volume of water, N_c is the particle number density, and $(R_p)_{ss}$ is the reaction rate at steady state. Results are reported in Figure 10. The agreement between the values deduced from the two sets of experimental data is very good indeed.

The data of Lichti and co-workers were originally used to determine the volume dependence of free-radical entry in styrene emulsion polymerizations. In the approach adopted by these authors[22,23] the PSD was found to be dependent on both ρ, k, and K at the same time. Within this theoretical framework, the kinetic behavior and the PSD time evolution could be considered independent of each other. Accordingly, from an appropriate combination of experimental determinations, in principle, it might be possible to determine the values of ρ, $\bar{n}$, and K as well as the volume dependences of the various rate coefficients governing particle growth. On the contrary, according to the approach presented in this paper, PSD depends only on ρ and $K\bar{n}$. Consequently, in the analysis of systems having $\bar{n}_{ss} \leq 1/2$, it turns out that PSD and kinetic data at steady state are not independent of each other. The reasoning is the following. When the experimental data are fit at t = 35 min, practically the value of $K\bar{n}$ is already predetermined by requiring that the mean volume predicted theoretically coincides, within experimental error, with that observed experimentally. This requirement is due to the experimental $\mathbf{n}(v,t)$, which is much more accurate around the mean or at the maximum of the PSD. The value of ρ is then fitted by making the predicted and observed PSD coincide as closely as possible. However, in the stationary state, for systems conforming to the zero–one kinetics $\rho(v)$ and $k(v)$ are not independent of each other since

$$\bar{n}_{ss} = \frac{\rho(v)}{2\rho(v) + k(v)} \tag{55}$$

Accordingly, once a steady-state value of R_p is reached (no matter whether it is an apparent or a true steady state), $\rho(v)$ and $k(v)$ behave no longer independently of each other (at least as far as PSD is concerned). In other words, if we assume a certain volume dependence for the entry constant, from the analysis of PSD we shall find the same dependence for the exit constant and vice versa. This means that PSDs of systems having $\bar{n}_{ss} \leq 1/2$ are per se insensitive to any mechanistic assumption concerning the rate constants. In this connection, very recently, an alternative approach based on the effect of PSD on MWD has been proposed.[39] This method seems to work well for continuous polymerization systems having a low number of growing radicals per particle. It provides a simple tool for estimating the volume dependence of the entry rate constant.

Conclusions

The model developed in this paper gives expressions for the time evolution of PSDs in the SE Interval II that are easy to evaluate. The core of this approach relies on reducing the infinite set of SE equations for particle growth by means of a suitable combination of transforms. Their choice results from a careful analysis of the symmetry of all the variables involved, i.e., the reaction time, t, the number, i, of growing radicals, and the size, v, of the particles. The results obtained represent a considerable consolidation of earlier theories in that (i) for systems conforming to the zero–one kinetics, a comprehensive description has been achieved; (ii) the contribution of latex particles having more than one growing radical has been accounted for properly; (iii) bimolecular termination has been explicitly included in the model (at least for systems where mutual annihilation between two growing radicals is not the main chain-stopping reaction); (iv) general expressions for the time evolution of the cumulants of the PSDs (both in the transient and nontransient cases) have been determined. These solutions not only revise theoretical misinterpretations that appeared in the scientific literature but also allow the rate coefficients to be extracted with more precision from reliable experimental data. In this connection it has been shown that the rate coefficients obtained from available PSD data are in excellent agreement with values taken from dilatometric kinetic studies.

Acknowledgment. I am deeply indebted to Prof. R. G. Gilbert of Sidney University for providing the original PSD data of styrene polymerization.

Appendix A. Solution of Equation 20

By application of the standard Fourier's method of variable separation, a general solution of eq 20 is

$$\Psi(s,x,t) = \sum_{\lambda} C(\lambda)(k - [k + sK]x)^{\eta} \times \exp\left\{\lambda t - \frac{\rho}{(k + sK)^2}[k - (k + sK)x]\right\} \tag{1A}$$

where

$$\eta = \frac{\rho k}{(k + sK)^2} - \frac{\lambda + \rho}{k + sK}$$

λ is a separation constant, and $C(\lambda)$ is a composite constant that may depend upon λ. The summation is extended over all values of λ, giving physically acceptable solutions. We now argue that

$$\eta \equiv 0, 1, 2, ..., n \equiv j \text{ (zero or positive integer)}$$

In this way all the derivatives of the generating function are finite at the points $s,x = 0$ and $x = 1$. Accordingly we have

$$\lambda t = (k/A - 1)\rho t - jAt \tag{2A}$$

where $A = k + sK$. Equation 1A can be recast into

$$\Psi(x,s,t) = \sum_j^{\infty} C(j)[k - Ax]^j \exp\{[\rho(k/A - 1) - jA]t - \rho/A^2(k - Ax)\} \quad (3A)$$

For a seeded system where $N_0(0) = 1$, at $t = 0$ the boundary condition states that

$$\sum_j^{\infty} C(j)[k - Ax]^j \exp\{-\rho/A^2[k - Ax]\} = \mathcal{L}^\circ(s)$$

or

$$\sum_j^{\infty} C(j)[k - Ax]^j = \sum_j^{\infty} \mathcal{L}^\circ(s)(\rho/A^2)^j\,[(k - Ax)^j]/j! \quad (4A)$$

When the coefficients of $(k - Ax)^j$ are equated, a general expression for $C(j)$ is obtained

$$C(j) = \mathcal{L}^\circ(s)\frac{1}{j!}(\rho/A^2)^j \quad (5A)$$

The substitution of eq 5A into eq 3A then finally gives eq 21. For a reacting system where the average number of growing radicals per particle has already reached its stationary-state value, the boundary conditions must be set at the point $x = 1$ and $t = 0$. Owing to the properties of the generating function Ψ, initial conditions are satisfied only for $j = 0$ so that

$$C = \mathcal{L}^\circ(s) \exp\{-\rho sK/A^2\} \quad (6A)$$

Inserting eq 6A into eq 3A, we obtain eq 23.

Appendix B. Solution of Equation 29

The method of variable separation can be used to solve eq 29. The function $\Psi(x,s,t)$ is assumed to be of the form $\Xi(x,s)\ T(t)$. Accordingly, the problem becomes that of solving the two ordinary differential equations

$$\frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t} = \lambda \quad (1B)$$

and

$$2c(1 - x)\mathrm{d}^2\Xi/\mathrm{d}x^2 + (k - Ax)\mathrm{d}\Xi/\mathrm{d}x + [\rho(x - 1) - \lambda]\Xi = 0 \quad (2B)$$

and then allowing the separation constant λ to take all values that are physically acceptable for the given reaction system. The solution of eq 1B is obviously

$$T(t) = B\exp(\lambda t) \quad (3B)$$

where B is a constant whose value may depend upon that of λ. Thus, the general solution for $\Psi(x,s,t)$ will be of the form

$$\Psi(x,s,t) = \sum_\lambda B(\lambda)\ \Xi(x,s) \exp(\lambda t) \quad (4B)$$

To discover the nature of the function $\Xi(x,s)$, we put $1 - x = \xi$ so that eq 2B can be readily transformed to

$$2c\xi\mathrm{d}^2\Xi/\mathrm{d}\xi^2 + (-A\xi + sK)\mathrm{d}\Xi/\mathrm{d}\xi - (\rho\xi + \lambda)\Xi = 0 \quad (5B)$$

In standard form, the differential equation 5B is of the type

$$(a_0x + b_0)\mathrm{d}^2y/\mathrm{d}x^2 + (a_1x + b_1)\mathrm{d}y/\mathrm{d}x + (a_2x + b_2)y = 0 \quad (6B)$$

According to Erdélyi,[40] a general solution of eq 6B is given in terms of confluent hypergeometric functions. In the present case the general solution of eq 5B is known to be

$$\Xi(\xi,s) = \exp(\epsilon\xi)\{P\,{}_1F_1[\alpha,\gamma;-\xi(D/2c)] + Q\xi^{1-\gamma}\,{}_1F_1[\alpha-\gamma+1,2-\gamma;\xi(D/2c)]\} \quad (7B)$$

where ${}_1F_1[a,b;x]$ denotes the confluent hypergeometric function of a variable x with parameters a and b, and

$$\epsilon = (A + D)/4c$$

$$D^2 = A^2 + 8\rho c$$

$$\alpha = (sK\epsilon - \lambda)/D$$

$$\gamma = sK/(2c)$$

We now argue that $Q = 0$. Our reasoning is that, from its definition, the function $\Psi(x,s,t)$ must be the sum of terms that contain only positive integral powers of x. Likewise, if the substitution $x = 1 - \xi$ is made, the function $\Xi(\xi,s)$ must also be the sum of the terms that contain only integral powers of ξ. Now the confluent hypergeometric function is known to be expressible as an infinite sum of terms containing only positive integral powers of the argument. Therefore, we argue that $Q = 0$ because, if this were not so, then the presence of the nonintegral power $\xi^{1-\gamma}$ would generate an infinite sum of terms containing nonintegral powers of ξ. Accordingly, turning back to the x variable and putting $Q = 0$ in eq 7B gives the general expression for the generating function Ψ

$$\Psi(x,s,t) = \sum_\lambda C(\lambda) \exp[-\epsilon(x - 1)]\,{}_1F_1[\alpha,\gamma;(x-1)D/(2c)] \exp(\lambda t) \quad (8B)$$

where $C(\lambda)$ is a composite constant whose possible dependence upon λ is emphasized when it is written as $C(\lambda)$.

For $x = 0$ the $\Psi(x,s,t)$ function represents the Laplace transform of the PSD of reaction loci in state 0. Since, for a seeded system where $N_0(0) = 1$, the Laplace transform of these distinctive latex particles should be a decreasing function of time, we argue that none of the physically acceptable values of λ can be positive. Moreover, the generating function Ψ must result from a finite combination of elementary functions. This holds because, at the point $x = 0$, we shall find the time-dependent Poissonian solution given by Blackley[35] to the locus population distribution $N_i(t)$. This condition is fulfilled only if the confluent hypergeometric function is expressible in terms of simple elementary functions. In this connection, it has been proved[40] that the confluent equation has a solution that is a finite combination of elementary functions *if and only if* either α or $\gamma - \alpha$ is an integer. This last conclusion, coupled to the constraint $\lambda < 0$, leads to the relationships

$$\gamma - \alpha = -n; \quad \lambda = sKA/(4c) - D[sK/(4c) + n] \quad (9B)$$

where n is a positive integer. Please note that since

$$D = (A^2 + 8\rho c)^{1/2}$$

the condition $\lambda < 0$ is met for every n. Thus, from eq 9B it follows that

$$\Psi(x,s,t) = \sum_{n=0}^{\infty} C(n) \exp[-\epsilon(x - 1)]\,{}_1F_1[sK/(2c)+n,sK/(2c);D(x-1)/(2c)] \exp\{[sKA/(4c) - D(sK/4c + n)]t\} \quad (10B)$$

To determine the values for the coefficients $C(n)$, initial boundary conditions must be considered. For a seeded system where, at reaction time $t = 0$, $N_0(0) = 1$, we have

$$\mathcal{L}^\circ(s)\exp[\epsilon(x-1)] = \sum_{n=0}^{\infty} C(n)\,{}_1F_1[sK/(2c)+n,sK/(2c);D(x-1)/(2c)] \tag{11B}$$

To find a general expression for the coefficients $C(n)$, first we express the exponential on the left-hand side of eq 11B by means of the confluent hypergeometric function[40]

$$\exp[\epsilon(x-1)] = {}_1F_1[sK/(2c),sK/(2c);lD(x-1)/(2c)] \tag{12B}$$

where $l = (2\epsilon c)/D$ is a multiplication parameter. As a second step we use the multiplication theorem

$${}_1F_1[a,b;lx] = l^{-a}\sum_{n=0}^{\infty}\frac{(a)_n}{n!}(1-l^{-1})^n\,{}_1F_1[a+n,b;x];\quad l > 1/2 \tag{13B}$$

where $(a)_n$ is the Pochammer symbol defined as

$$(a)_n = \Gamma(a+n)/\Gamma(a)$$

By applying eq 13B to the right-hand side of equation 12B, we have

$$\exp[\epsilon(x-1)] = [D/(2\epsilon c)]^{sk/(2c)}\sum_{n=0}^{\infty}\frac{[sK/(2c)]_n}{n!}\times [1-D/(2\epsilon c)]^n\,{}_1F_1[sK/(2c)+n,sK/(2c);D(x-1)/(2c)] \tag{14B}$$

Please note that, since $l = [(k + sK) + D]/(2D)$, the constraint $l > 1/2$ is fulfilled for every $c > 0$. Finally, rearranging eqs 12B, 13B, and 14B and equating on both sides the coefficients for ${}_1F_1[sK/(2c)+n,sK/(2c);D(x-1)/(2c)]$, we obtain the following expressing for the coefficient $C(n)$

$$C(n) = \mathcal{L}^\circ[D/(2\epsilon c)]^{sk/(2c)}\frac{[sK/(2c)]_n}{n!}[1-D/(2\epsilon c)]^n \tag{15B}$$

Thus, from eq 15B we have

$$\Psi(x,s,t) = \mathcal{L}^\circ(s)[D/(2\epsilon c)]^{sk/(2c)}\exp\{sK/(4c)[(k+sK) - D] - \epsilon(x-1)\}\sum_{n=0}^{\infty}\frac{[sK/(2c)]_n}{n!}[1-D/(2\epsilon c)]^n\times {}_1F_1[sK/(2c)+n,sK/(2c);D(x-1)/(2c)]\exp(-nDt) \tag{16B}$$

It is possible to obtain a simpler expression for the generating function. If we make use of the first Kummerer theorem

$${}_1F_1[a,c;x] = e^x\,{}_1F_1[c-a,c;-x]$$

and of the relationship

$${}_1F_1[-n,a;x] = \frac{n!}{(a)_n}L_n^{a}(x) \tag{17B}$$

where L_n^a are Laguerre polynomials, eq 16B reduces to

$$\Psi(x,s,t) = \mathcal{L}^\circ(s)[D/(2\epsilon c)]^{sk/(2c)}\exp\{[D/(2c)-\epsilon](x-1) + sK/(4c)[(k+sK) - D]t\}\sum_{n=0}^{\infty}[(1-D/2\epsilon c)e^{-Dt}]^n L_n^{\nu}[-D(x-1)/(2c)] \tag{18B}$$

where $\nu = sK/(2c) - 1$. The infinite summation on the right-hand side corresponds to the generating function for the Laguerre polynomials.

$$\sum_{n=0}^{\infty}L_n^{a}(x)z^n = (1-z)^{-(a+1)}\exp[xz/(z-1)] \tag{19B}$$

Accordingly, the final expression for the generating function $\Psi(x,s,t)$ is

$$\Psi(x,s,t) = \mathcal{L}^\circ(s)[D(1-z)/(2\epsilon c)]^{sK/(2c)}\times \exp\left\{\frac{[D/(2c)-\epsilon]}{1-z}(x-1) + sK/(4c)[(k+sK)-D]t\right\} \tag{20B}$$

where $z = [1 - D/(2\epsilon c)]e^{-Dt}$. For $s = 0$, eq 20B gives

$$\Psi(x,0,t) = \exp\left\{\left[\frac{2\rho}{h+k} + \frac{(h-k)e^{-ht}}{(h-k)e^{-ht} + (h+k)}(h/c)\right](x-1)\right\} \tag{21B}$$

By expression of the exponentials in terms of hyperbolic circular functions and by use of the associated multiplication formulas of the arguments, after some tedious algebra, eq 21B reduces to eq 30b. This equivalence can be proven also by simple numerical analysis.

For a reacting system that at time $t = 0$, has already reached the stationary state of the $N_i(t)$ distribution, initial conditions are given at the point $s = 0$ and $x = 1$. In this case, at reaction time $t = 0$, from eq 10B we have

$$\mathcal{L}^\circ(s) = \sum_{n=0}^{\infty}C(n) \tag{22B}$$

so that the coefficients $C(n)$ are not unequivocally determined. However, physically, we do know that for the system under consideration there is one and only one solution. Therefore, only one value of n gives a physically acceptable solution. This is a direct consequence of the fact that for $s = 0$ the Ψ function reduces to the generating function for the locus population distribution $N_i(\infty)$. Of course this function must be time independent. A close inspection of eq 10B indicates that this conditions is fulfilled only for $n = 0$. Accordingly, since $C = \mathcal{L}^\circ(s)$ and

$${}_1F_1[sK/(2c),sK/(2c);D(x-1)/(2c)] = \exp[D(x-1)/(2c)]$$

from eq 10B, we obtain immediately eq 31.

Appendix C. Solutions of Equation 47

Since no general formula for the inversion of eq 47 is available even in the most extensive tabulation of Laplace transforms,[41] we proceed as follows. Taking derivatives of both sides of eq 47 with respect to time and expanding the exponential on the right-hand side, we have

$$\mathcal{L}\left\{\frac{\partial}{\partial t}\mathbf{n}(\upsilon,t)\right\} = -2\rho s\mathcal{L}^\circ(s)\left\{\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\frac{(2st)^n}{R(s+\beta)^{n+1}}\right\} \tag{1C}$$

where $R(s+\beta)$ is a function of the variable $s + \beta$ only

$$R(s+\beta) = [(s+\beta)^2 + a^2]^{0.5} + (s+\beta) \tag{2C}$$

Furthermore, owing to the shift theorem

$$\mathcal{L}^{-1}[1/R^{n+1}(s+\beta)] = \frac{(n+1)}{a^{n+1}}\left\{\frac{1}{\upsilon}e^{-\beta\upsilon}J_{n+1}(a\upsilon)\right\} \equiv f_{n+1}(\upsilon) \tag{3C}$$

In the limit $\upsilon \rightarrow 0$ for the function $f_{n+1}(\upsilon)$ and its rth derivative we have

$$\lim_{\upsilon\rightarrow 0}\frac{1}{\upsilon}e^{-\beta\upsilon}J_{n+1}(a\upsilon) = 0$$

$$\lim_{v \to 0} f^{(r)}{}_{n+1}(v) = 0; \quad r < n$$

Accordingly we can write

$$\mathcal{L}^{-1}\{s^n/R^{n+1}\} = (n+1)/a^{n+1} f^{(n)}{}_{n+1}(v) \qquad (4C)$$

Finally, since

$$\mathcal{L}^{-1}[s\mathcal{L}^\circ(s)] = \frac{\mathrm{d}}{\mathrm{d}v}[\mathbf{n}(v,0)] \qquad (5C)$$

the inverse Laplace transform on the right-hand side of eq 1C is given by the convolution integral between eqs 5C and 4C. Integration with respect to time then finally gives eq 48. In the other solution to eq 47 both sides are derived first with respect to c, and then the exponential on the right-hand side is expanded to give

$$\mathcal{L}\left[\frac{\partial}{\partial c}\mathbf{n}(v,t)\right] = 8(\rho^*)^2\mathcal{L}^\circ(s)\sum_{n=0}^{\infty}\frac{(-2\rho t)^n}{n!}\frac{s^{n+1}}{rR^{n+2}} \qquad (6C)$$

where $r = [(s + \beta)^2 + a^2]^{1/2}$. The further steps are equal to those adopted in the previous solution, so that, finally, integrating with respect to c, we obtain eq 50.

References and Notes

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(41) The author would be happy to receive a methodology for transforming the integral inversion of eq 47 into simpler functional forms.