A Mathematical Model of Mixing and Polymerization in a Semibatch Stirred-Tank Reactor

Güray Tosun
Central Research & Development, Science & Engineering Laboratories, E. I. du Pont de Nemours & Co., Inc.,
Wilmington, DE 19880

Effects of mixing on number- and weight-average degree of polymerization in free radical homopolymerization in solution in a semibatch stirred tank-reactor have been modeled by use of the "partially segregated feed" model of Villermaux (1989) and the lumped kinetic treatment of addition polymerization. Mixing conditions are described in terms of the dimensionless time constants θ_M and θ_X for convective and diffusive mixing, respectively. Results show that DP_n is relatively insensitive, while DP_w is highly sensitive to mixing conditions. Comparison with ideal mixing results shows that polydispersity (DP_w/DP_n) can rise greatly as mixing becomes increasingly nonideal, depending on the value of dimensionless flow rate and dimensionless initiator rate constant. Time constants of the mixing model need to be expressed as dimensional correlations before the proposed polymerization model can be compared to experimental measurements. The model may be adapted to melt polymerization in nonideal CSTR such as LDPE.

Introduction

Nonideal mixing conditions in stirred-tank reactors are often suspected to be related to unexpectedly broad chain length distribution (molecular weight distribution) in free radical chain growth polymerizations. It is difficult to investigate this problem experimentally. There have been relatively few attempts to model polymerization and mixing mathematically in stirred-tank reactors, even though theory and mathematical treatments of mixing itself have advanced greatly in recent years. A literature search back to 1960 produced a few models of mixing and polymerization in general, but almost none for stirred-tank reactors relating molecular weight and molecular weight distribution (MWD) to mixing.

One problem with modeling polymerization and mixing in batch or semibatch stirred tanks is that the viscosity rise due to polymerization quickly changes the initial assumptions regarding the extent and homogeneity of turbulence which govern micromixing aspects of the mixing process. Another potential problem for stirred-tank reactors in general is the difficulty of combining the mathematical complexities of detailed polymerization kinetics with a mixing model that is itself often quite involved. Using lumped kinetic models and the moments of the molecular weight distribution, however, one can greatly simplify the mathematics of polymerization, while still being able to calculate concentrations and number- and weight-average degree of polymerization, which in many instances would constitute sufficient information regarding the effects of mixing on polymerization. Nevertheless, lumped kinetic treatment still requires several reaction and moment rate equations (depending on the complexity of the polymerization mechanism) that must be simultaneously solved with the mixing model equations. In the case of the more recent turbulence (k-ϵ) models, introducing even this level of mathematics for describing the kinetics creates problems of excessive computation times.

Perhaps partly due to the reasons discussed above, studies of the effect of mixing on polymerization reactions in stirred-tank reactors up to now have been confined mainly to treatments of the extremes of mixing, that is, complete microsegregation and complete micromixing. Such studies have been carried out by Thiele and Breme (1988), Baade et al. (1982), Harada et al. (1968), Tadmor and Biesenberger (1966). Reviews of this type of treatment may be found in Rao and Edwards (1973) and Nauman (1974).

Notable studies not confined to the extremes of mixing are the following. Lee and Lee (1987) studied the effect of mixing on conversion in a fast step growth polymerization in a stirred adiabatic batch reactor. They explained their experimental results using a stationary slab model based on diffusion and reaction as the slab was stretched by the action of elongational shear. The slab was assumed to contain one reactant in one-half and the other in the remaining half initially. Using dimensional analysis, they introduced four characteristic times to describe the interactions of mixing, diffusion and chemical reaction. They did not consider aspects of polymerization other than conversion. Atiqullah and Nauman (1990) presented (for a continuous stirred-tank reactor) a model based on stretching striations, residence time distribution, and transient diffusion between striations and an interstitial fluid with average composition. They then related their two mixing parameters to the copolymer composition distribution, but not to the degree of polymerization (DP) or MWD.

Chella and Ottino (1983) and Fields and Ottino (1987) modeled diffusion and polymerization reactions within lamellar striations in reaction injection molding (RIM). They assumed only lamellar stretching motion and no convection, in their respective studies. They computed (among other things) conversions and molecular weight as functions of time, striation thickness and lamellar space. Marini and Georgakis (1984a,b) modeled steady-state polymerization of LDPE in a continuous stirred-tank reactor as three CSTRs-in-series with recycle. They related polydispersity (DP_w/DP_n) to polymer temperature, feed rate, and solvent concentration for ideal CSTR and for the nonideal model. The variables describing mixing were the volume of the two small CSTRs, representing the semisegregated initiator feed zone, and the recirculation flow rate between the bulk and the semisegregated feed zone. Numerical values for these were estimated from the internal flow velocity and the nozzle diameter for only one set of conditions. No attempt was made to relate polymer properties to different mixing conditions. Since internal flow in stirred tanks is related mainly to macromixing, this model does not seem to take into account micromixing. Furthermore, it cannot be applied to the case of semibatch operation.

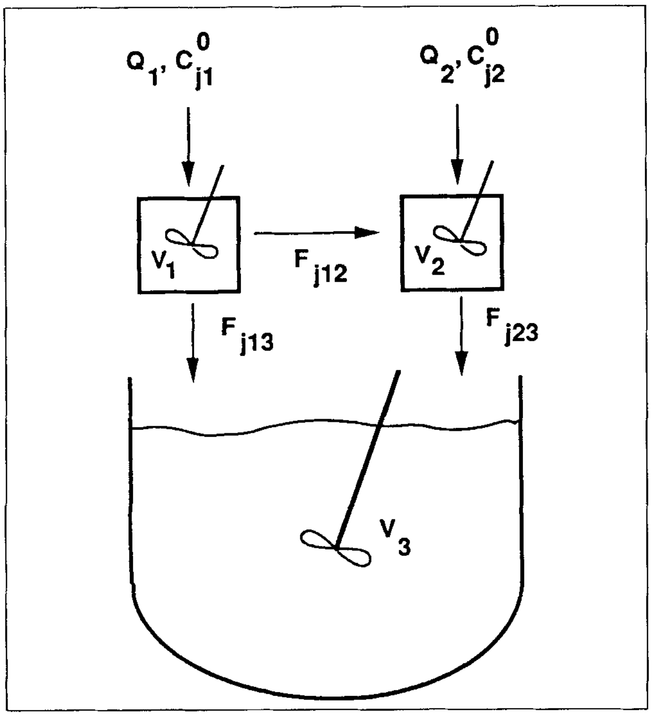

Figure 1. Schematic diagram of segregated feed mixing model (Villermaux, 1989).

In summary, there appears to be no mathematical model of the effects of mixing on polymer MWD, that is, DP_n, DP_w, capable of covering the entire range of mixing conditions from ideal mixing to complete segregation in stirred-tank (semibatch or continuous) reactors.

In the present work, free radical chain homopolymerization (in solution) and mixing in a semibatch stirred-tank reactor with two feed streams was modeled by combining the recent segregated-feed-zone mixing model of Villermaux (1989) and the well known lumped-chain-concentration model of the polymerization kinetics (Ray, 1972). The objective was to relate number- and weight-average degree of polymerization (DP_n, DP_w), calculated from the moments of the MWD, to mixing conditions expressed in terms of the time constants of the mixing model. The present treatment is limited to polymerization in solution where the polymer concentration is relatively low such that viscosity does not rise appreciably. A typical example of such a situation is methyl methacrylate polymerization in solvent. However, a steady-state, continuous stirred-tank version of the model can easily be formulated and applied to melt polymerizations with constant steady-state viscosity under turbulent mixing conditions, such as LDPE polymerization in continuous stirred-tank reactors.

The present treatment is also subject to the limitations of the mixing model as will be discussed below.

Model for Mixing

The segregated-feed-zone model proposed by Villermaux (1989) was applied in the present work to the case of semibatch stirred-tank reactor with two separate feed streams being fed into the reactor that initially contains solvent without reactants. This model has elements similar to those of Murakami et al. (1981), Pohorecki and Baldyga (1983) and the IEM (interaction by exchange with the mean) model (Harada et al., 1962; Costa and Trevissoi, 1972; Villermaux and Devillon, 1972). Figure 1 shows a schematic description of the model. The two small volumes V_1 and V_2 represent the semisegregated feed zones that receive feed flows Q_1 and Q_2 and exchange mass with the rest of the reactor volume V_3 and with each other by means of the mass-transfer mechanisms provided by the model. Mathematical representation of the model is shown below.

Volumes

$$\frac{dV_1}{dt} = Q_1 - \frac{V_1}{t_m} \tag{1}$$

$$\frac{dV_2}{dt} = Q_2 - \frac{V_2}{t_M} \tag{2}$$

$$\frac{dV_T}{dt} = Q_1 + Q_2 \tag{3}$$

$$V_T = V_1 + V_2 + V_3 \tag{4}$$

Mass balances of species j in three zones

$$\frac{d(V_1 C_{j1})}{dt} = R_{j1} V_1 + Q_1 C^0_{j1} - F_{j13} - F_{j12} \tag{5}$$

$$\frac{d(V_2C_{j2})}{dt}=R_{j2}V_2+Q_2C^0_{j2}-F_{j23}+F_{j12} \tag{6}$$

$$\frac{d(V_3C_{j3})}{dt}=R_{j3}V_3+F_{j13}+F_{j23} \tag{7}$$

Mixing or mass-transfer terms between zones

$$F_{j13}=\frac{V_1C_{j1}}{t_M}+\frac{V_1(C_{j1}-C_{j3})}{t_1} \tag{8}$$

$$F_{j23}=\frac{V_2C_{j2}}{t_M}+\frac{V_2(C_{j2}-C_{j3})}{t_2} \tag{9}$$

$$F_{j12}=\frac{(V_1+V_2)(C_{j1}-C_{j2})}{t_{12}} \tag{10}$$

Above equations mathematically reduce to the case of perfect mixing when the time constants t_M and t_X ($X = 1, 2$) go to zero. Then, the equations simply become those describing an ideal semibatch reactor:

$$\frac{dV_T}{dt}=Q_1+Q_2 \tag{11}$$

$$\frac{d(V_TC_j)}{dt}=R_jV_T+Q_1C^0_{j1}+Q_2C^0_{j2} \tag{12}$$

Conversely, when the time constants increase without bounds, the equations reduce to the case of total segregation with no exchange and reaction.

In the present application of the model, it was assumed that the initiator feed solution flowed into zone V_1 with flow rate Q_1 and the monomer feed solution flowed into feed zone V_2 with flow rate Q_2. Also, in the present application the subscript j indicates the species being chemically produced or consumed as well as additive linear functions of their concentrations, such as the moments of the MWD. The chemical reaction rate terms R_j must be specified for the polymerization system being modeled. In the present case, they have been provided by means of a kinetic model for the free radical addition polymerization.

Villermaux (1989) does not elaborate on the physical aspects of the model. However, judging by the equations of the model, it can be concluded that the model is based on the concept of segregated homogeneous zone(s) of feed(s) exchanging material with the remaining volume of the reactor vessel by two mechanisms:

(1) Erosion of the segregated volume presumably by bulk flow and turbulent diffusion with a characteristic time constant t_M.

(2) Mass exchange across the interface by a mechanism similar to diffusive mass transfer involving concentration gradients across an interface.

This exchange has a characteristic time constant, t_1 or t_2, which is functionally equivalent to $1/kA$ in mass transfer. As shown in Figure 1, there can also be a diffusive mass exchange mechanism between the segregated feed zones 1 and 2, characterized by a time constant, t_{12}. However, the presence of this mechanism would require interface contact or direct mixing between the two feed zones.

Since the erosion of the feed zone by bulk flow and turbulent diffusion would have to be followed by a diffusive mass-transfer step, which should be much faster than the convection process in a low-viscosity turbulent environment, it is assumed that the decay rate of the segregated volume is governed mainly by convection and that t_M in the model equations includes the overall combined action of convective (macro) and diffusive (micro) mixing. The segregated zones are not totally segregated as in the model of Pohorecki and Baldyga (1983a,b), but permit mass transfer across the interface, as discussed above. The mixing zone, volume 3, grows in time as was implied in Pohorecki and Baldyga (1983) and IEM models.

As for the values of time constants, no definite correlations have been offered, but it has been suggested (Villermaux, 1989) that t_M should be proportional to the internal circulation time t_c and that t_X can be taken to be the eddy lifetime as proposed by Baldyga and Bourne (1984). In a more recent report, Muhr et al. (1990) presented empirical correlations for these time constants obtained by fitting the model to diazo coupling reactions. The present author believes that Pohorecki and Baldyga's (1983b) correlations for their time constants t_M and $t_{md} = 1/2\ k_{md}$ are probably the most reasonable initial starting values, since the P&B model employs rather similar mechanisms for decay of the segregated volumes and for diffusive mass exchange. Actual values to be used for a specific situation would have to be obtained by numerical fitting. The interzone exchange time constant t_{12} is perhaps the least well defined one. One way to handle this problem is to assume that the feeds are spatially well enough apart that this time constant may be set equal to infinity.

This mixing model was chosen because it is mathematically simple but physically plausible and theoretically related to previous mixing model concepts as mentioned above. It differs from the model of Marini and Georgakis (1984a,b) in that (i) the volumes of the feed zones of the Villermaux model grow during feeding and decay afterwards exponentially for the case of semibatch reactor which cannot be treated by the former model; (ii) each feed zone exchanges mass with the bulk as well as the other feed zone by convective and diffusive mechanisms, the main elements of turbulent mixing, as opposed to convection (internal recycle) alone, which is the case for the former model. It should be noted that Villermaux (1989) was able to show good agreement in trends with three real systems using the dimensionless formulation of the mixing model.

Kinetic Model for Free Radical Addition Polymerization

Free radical chain addition polymerization in its simplest form, that is, without branching or transfer, and with disproportionation as the only chain termination mechanism was selected as the model polymerization reaction for its relative mathematical simplicity. The generally accepted (lumped) treatment (Ray, 1972; Villermaux and Blavier, 1984) shown below was followed:

Initiation

$$I \xrightarrow{k_d} 2A$$

$$A+M \xrightarrow{k_i} R_1$$

Propagation

$$R_n + M \xrightarrow{k_p} R_{n+1} \tag{13}$$

Termination

$$R_n + R_m \xrightarrow{k_{td}} M_n + M_m$$

where

I = initiator
A = initiated radical
R_n = growing (radical) polymer of length n
M_n = dead polymer of length n
k_d, k_i, k_p, k_{td} = rate constants for initiation, monomer activation, polymerization, and termination by disproportionation

Kinetic equations

The kinetic equations for the above system are as follows. For initiator:

$$\frac{dI}{dt} = -k_d I \tag{14}$$

$$\frac{dA}{dt} = 2fk_d I - k_i AM \tag{15}$$

For growing polymer:

$$\frac{dR_1}{dt} = k_i AM - k_p R_1 M - k_{td} RR_1 \tag{16}$$

$$\frac{dR_n}{dt} = k_p (R_{n-1} - R_n) M - k_{td} RR_n \qquad n \geq 2 \tag{17}$$

$$\frac{dR}{dt} = k_i AM - 2k_t R^2 \tag{18}$$

where $R = \sum_{n=1}^{\infty} R_n$ is the total concentration of the growing polymer and $k_t = 1/2\ k_{td}$ to follow convention.

For monomer and dead polymer:

$$\frac{dM}{dt} = -k_i AM - k_p RM \tag{19}$$

$$\frac{dM_n}{dt} = k_{td} RR_n \tag{20}$$

and defining $P = \sum_{n=1}^{\infty} M_n$ = total concentration of dead polymer

$$\frac{dP}{dt} = 2k_t R^2 \tag{21}$$

Making the quasi-steady-state approximation (QSSA) for the free radical species:

$$k_i AM = 2fk_d I \tag{22}$$

$$R = \left(\frac{fk_d I}{k_t}\right)^{1/2} \tag{23}$$

and

$$\frac{dP}{dt} = 2fk_d I \tag{24}$$

and application of long-chain hypothesis (LCH) to Eq. 19 yields:

$$\frac{dM}{dt} = -k_p \left(\frac{fk_d}{k_t}\right)^{1/2} MI^{1/2} \tag{25}$$

Initiator efficiency f was taken to be unity in the present work to simplify things.

The moments of the MWD were derived from the general definition:

$$\lambda_k = \sum_{n=1}^{\infty} n^k M_n \tag{26}$$

by use of the method of moment generating function (Ray, 1972). The results, in terms of time derivatives of the first three moments, are:

$$\frac{d\lambda_0}{dt} = 2k_t R^2 \tag{27}$$

$$\frac{d\lambda_1}{dt} = 2k_t \left(\frac{1}{1-p}\right) R^2 \tag{28}$$

$$\frac{d\lambda_2}{dt} = 2k_t \left[\frac{1+p}{(1-p)^2}\right] R^2 \tag{29}$$

where

$$p = \frac{k_p M}{k_p M + 2k_t R} \tag{30}$$

is the probability of propagation. Number- and weight-average degree of polymerization were then calculated from the relations (Ray, 1972):

$$DP_n = \frac{\lambda_1}{\lambda_0} \tag{31}$$

$$DP_w = \frac{\lambda_2}{\lambda_1} \tag{32}$$

and polydispersity ratio Z_p was calculated from:

$$Z_p = \frac{DP_w}{DP_n} \tag{33}$$

The rate expressions given in Eqs. 14, 24, 25 and 27-29 were used for the rate terms R_{ji} in the mixing model (Eqs. 5-7). Note that the model equations were applied to I, M, P, and the first and second moments as pseudo components. λ_0 is by definition equal to P. It can be shown that treating λ_1 and λ_2 as pseudo components is mathematically valid because of the definition of the moments and the volumetric additivity of the moments, again a consequence of their definition.

To begin with, QSSA was not made, and a separate model equation was derived for R (total concentration of the growing polymer chains) where the chemical rate term would be Eq. 18. However, numerical computations revealed an extremely stiff situation where stable solutions were not possible. For the dimensionless treatment of the model, a criterion test was devised for valid approximate application of QSSA. It was shown that under real polymerization conditions quasi-steady-state assumption for the free radical species in all three zones is quite reasonable.

Dimensionless Model

To reach general conclusions from the model, while avoiding the problem of fixing specific values for the mixing time constants, the model given above was reformulated with dimensionless variables.

The equations of the mixing model were made dimensionless by the variable transformations suggested by Villermaux (1989):

$$\hat{V}=V/V_o=V/V_T(0);\ \theta=t/t_o;\ \hat{Q}=\frac{t_oQ}{V_o};$$

$$\hat{C}_j=C_j/C_o;\ \text{and}\ \hat{R}_j=R_jt_o/C_o.$$

where

t_o = reference time scale
C_o = reference concentration
V_o = reference volume

The dimensionless equations are:

$$\frac{d\hat{V}_1}{d\theta}=\hat{Q}_1-\frac{\hat{V}_1}{\theta_M} \tag{34}$$

$$\frac{d\hat{V}_2}{d\theta}=\hat{Q}_2-\frac{\hat{V}_2}{\theta_M} \tag{35}$$

$$\hat{V}_T=\hat{V}_1+\hat{V}_2+\hat{V}_3 \tag{36}$$

$$\frac{d\hat{V}_T}{d\theta}=\hat{Q}_1+\hat{Q}_2 \tag{37}$$

$$\frac{d}{d\theta}(\hat{V}_1\hat{C}_{j1})=\hat{R}_{j1}\hat{V}_1+\hat{Q}_1\hat{C}^0_{j1}-\hat{F}_{j13}-\hat{F}_{j12} \tag{38}$$

$$\frac{d}{d\theta}(\hat{V}_2\hat{C}_{j2})=\hat{R}_{j2}\hat{V}_2+\hat{Q}_2\hat{C}^0_{j2}-\hat{F}_{j23}+\hat{F}_{j12} \tag{39}$$

$$\frac{d}{d\theta}(\hat{V}_3\hat{C}_{j3})=\hat{R}_{j3}\hat{V}_3+\hat{F}_{j13}+\hat{F}_{j23} \tag{40}$$

where

$$\hat{F}_{j13}=\frac{\hat{V}_1\hat{C}_{j1}}{\theta_M}+\frac{\hat{V}_1(\hat{C}_{j1}-\hat{C}_{j3})}{\theta_1} \tag{41}$$

$$\hat{F}_{j23}=\frac{\hat{V}_2\hat{C}_{j2}}{\theta_M}+\frac{\hat{V}_2(\hat{C}_{j2}-\hat{C}_{j3})}{\theta_2} \tag{42}$$

$$\hat{F}_{j12}=\frac{(\hat{V}_1+\hat{V}_2)(\hat{C}_{j1}-\hat{C}_{j2})}{\theta_{12}} \tag{43}$$

where

$$\theta_M=t_M/t_o$$
$$\theta_x=t_x/t_o\ (X=1,2)$$
$$\theta_{12}=t_{12}/t_o$$

Note that in the present application of the model t_M, t_1, and t_2 (t_x) were assumed to be constant for all species including the dead polymer chains. A more realistic, but more complicated, treatment may be to make t_1 and t_2 dependent on molecular size. It was felt that at this stage of development of the model where t_X and t_M are not provided as functions of system variables, adding this complexity would be unwarranted. The time constant t_{12} between the two feed zones was assumed to be infinity for reasons given in the earlier discussion of the (dimensional) model.

For the variable transformations above, the reference concentration C_o was taken to be M_o, monomer concentration in the monomer feed stream. The reference time t_0 was chosen to be proportional to a pseudo half-life for the monomer for the hypothetical case of undiluted feed streams reacting to form long-chain polymer where the initiator concentration remains close to its initial value:

From $$\ln\frac{M}{M_o}\cong\left(\frac{fk_p^2k_dI_o}{k_t}\right)^{1/2}t$$

$$t_{1/2}\cong\frac{\ln 2}{k_o}=\ln 2\left(\frac{k_t}{fk_p^2k_dI_o}\right)^{1/2}$$

t_0 was then taken to equal $1/k_o$, for simplicity:

$$t_0=\frac{1}{k_o}\ \alpha t_{1/2} \tag{44}$$

where

$$k_o=\left(\frac{fk_p^2k_dI_o}{k_t}\right)^{1/2} \tag{45}$$

is the pseudo-first-order rate constant for monomer consumption for the hypothetical case. The reference volume V_o was taken to be the initial volume of the solvent in the reactor.

Thus, for j = 1, 2, 3, the dimensionless rate equations for $\hat{I}$, $\hat{M}$, and $\hat{P}$ become (volume subscripts omitted):

$$\hat{R}_1=\frac{d\hat{I}}{d\theta}=-K_D\hat{I} \tag{46}$$

$$\hat{R}_2 = \frac{d\hat{M}}{d\theta} = -\Phi_o^{1/2}\hat{I}^{1/2}\hat{M} \tag{47}$$

$$\hat{R}_3 = \frac{d\hat{P}}{d\theta} = 2fK_D\hat{I} \tag{48}$$

where $K_D = k_d/k_o$ and $\Phi_o = M_o/I_o$.
The moments of the MWD were given by the following relationships derived from Eqs. 27–29:

$$\hat{\lambda}_o = \hat{P} \tag{49}$$

$$\hat{R}_4 = \frac{d\hat{\lambda}_1}{d\theta} = \Phi_o^{1/2}\hat{I}^{1/2}\hat{M} \tag{50}$$

$$\hat{R}_5 = \frac{d\hat{\lambda}_2}{d\theta} = 2fK_D\hat{I} + 3\Phi_o^{1/2}\hat{I}^{1/2}\hat{M} + \left(\frac{\Phi_0}{fK_D}\right)\hat{M}^2 \tag{51}$$

The equations of dimensionless model (Eqs. 34–40) were solved for $j = 1, 2, 3, 4, 5$, which made a total of 19 equations with Eqs. 41 and 42 (for $j = 1$-5) for the mixing terms and Eqs. 46–48, 50 and 51 for the rate terms inserted in their respective positions.

For the case of ideal mixing, mass balance:

$$\frac{d}{d\theta}(\hat{V}_T\hat{C}_j) = \hat{R}_j\hat{V}_T + \hat{Q}_1\hat{C}^o_{j1} + \hat{Q}_2\hat{C}^o_{j2} \tag{52}$$

along with Eq. 37 were sufficient to describe the ideal semibatch reactor system.

Analysis of QSSA

Strictly speaking, one can no longer make the quasi-steady-state approximation for the free radical species in the three zones of the present model. After consideration of each free radical species A to R_n, one can write differential equations for the total free radical concentration R' defined by:

$$R' = A + \sum_{n=1}^{\infty} R_n = A + R$$

for each zone as in Eqs. 38–40. For instance, for zone V_2:

$$\frac{d(\hat{V}_2\hat{R}_2')}{d\theta} = 2fK_D\hat{I}_2\hat{V}_2 - 2K_T(\hat{R}_2')^2\hat{V}_2 - \frac{\hat{V}_2\hat{R}_2'}{\theta_M} - \frac{\hat{V}_2(\hat{R}_2' - \hat{R}_3')}{\theta_2} \tag{53}$$

where $K_T = k_t/k_o$.

These differential equations would then have to be solved simultaneously with Eqs. 38–40 for other species. This was tried initially only to find extreme stiffness in the system that made stable solutions impossible. The error introduced by making the QSSA was then analyzed as follows: for each zone, the ratio between the transport terms ($\hat{F}_{jik}$ in Eqs. 41 and 42) and the chemical consumption term was defined as:

$$\Gamma_1 = \frac{\hat{F}_{j13}}{2K_T\hat{R}'^2_1} \tag{54}$$

$$\Gamma_2 = \frac{\hat{F}_{j23}}{2K_T\hat{R}'^2_2} \tag{55}$$

$$\Gamma_3 = \frac{\hat{F}_{j13} + \hat{F}_{j23}}{2K_T\hat{R}'^2_3} \tag{56}$$

where $j = 4$ for $\hat{R}'$.

Then, $\hat{R}_j'$ in numerator and denominator of each equation above was replaced with the QSSA value $(fK_D\hat{I}_i/K_T)^{1/2}$, and the value of Γ_i was calculated as a function of time simultaneously with the QSSA solution for the particular run. It was found for all runs in all four example cases that over the entire time range of the simulation ($0 - \theta_B$):

$$\Gamma_2 > \Gamma_1 > \Gamma_3$$

and that $\Gamma_2 \leq 0.01$ provided that $k_t/k_p \geq 10^4$ which is commonly the case in actual free radical polymerizations. This analysis established that, at least for the example cases of this study, dropping the transport term $\hat{F}_{jik}$ in equations like Eq. 53 for all three zones ($i = 1, 2, 3$) and setting righthand side equal to zero (QSSA) introduces an error of no more than 1% in the mass balances of the total free radical concentration. QSSA was, therefore, assumed to be a good approximation in solving the model equations for cases of practical interest.

Discussion of Results

Equations 34–43 and 52 with $j = 1$-5 for $\hat{I}$, $\hat{M}$, $\hat{P}$, λ_1, λ_2 were solved by a combination of analytical and numerical techniques. The solution consisted of three separate stages: (1) from start to end of feed flows; (2) from end of feed flows to decay of feed zone volumes to 0.1% of initial values; and (3) from end of stage 2 to end of batch time θ_B. The dimensionless parameters that defined the semibatch process with two feed streams were: flow rates $\hat{Q}_1$, $\hat{Q}_2$; feed time θ_F; batch time θ_B; kinetic ratio K_D; feed concentration ratio Φ_0; and the time constants for the mixing transport terms θ_M, θ_1, θ_2, and θ_{12}. For the sake of simplicity, f was assumed to be unity and the feed flow rates taken to be identical. Feed time, that is, the duration of the feed period was determined from the assumption that in every run the final volume would be 50% higher than the initial volume. Thus,

$$\theta_F = \frac{0.25}{\hat{Q}}$$

since

$$2\hat{Q} \times \theta_F = 0.50.$$

The interfeed mass exchange time constant (θ_{12}) was set to be effectively equal to infinity for reasons explained above. The time constants θ_M, θ_1, and θ_2 were assumed to be constant as discussed previously based on the assumption of nearly constant diffusivity in all three zones. Furthermore, θ_1 and θ_2 were also assumed to be identical, which is reasonable based on symmetry and equal feed rates in the vessel, provided that dilute monomer feed is used. Thus, θ_X in the rest of this discussion is to denote the dimensionless diffusive mixing time constants θ_1 or θ_2.

Table 1. Summary of Cases Modeled

Case No.	$\hat{Q}_F$	Φ_o	K_D	$(DP_n)_i$	$(Z_p)_i$	θ_F	θ_B
1	0.001	100	0.100	49.5	2.1	250	500
2	0.001	100	0.010	51.6	3.9	250	500
3	0.001	50	0.100	24.8	2.2	250	500
4	0.100	100	0.100	50.0	4.0	2.5	500

Table 2. Sample Results for Case 1

θ_X	θ_M	DP_n	Z_p	X_m
0	0	49.5	2.1	0.99
0.1	0.1	49.5	2.6	0.99
1.0	1.0	49.5	7.0	0.99
5.0	5.0	49.4	23.0	0.99
10.0	10.0	49.3	39.4	0.99
0.1	10.0	49.5	2.1	0.99
10.0	0.1	49.5	4.1	0.99

To handle the case of varying viscosity, one has to have an expression for t_X (t_1, t_2) as a function of viscosity. Until such expressions can be developed, one can use estimates such as the Pohorecki and Baldyga (1983b) expression (Eq. 58) or as suggested by Villermaux (1989), the eddy life time as proposed by Baldyga and Bourne (1984):

$$t_X \sim t_w = 12(\nu/\epsilon)^{1/2}$$

Since t_M is related to bulk convection and turbulent diffusion, it need not be related to viscosity.

The dimensionless batch time θ_B was set to a value long enough to produce essentially complete conversion of the monomer M. This value was 500 dimensionless time units. The mixing time constants θ_X, θ_M, kinetic constants K_D, Φ_0, and the flow rate $\hat{Q}$ were the parameters that governed the results of the calculations of concentrations, DP_n, and DP_w as functions of time. To focus on the effects of the mixing parameters θ_X and θ_M on the results, four sets of fixed values of K_D, Φ_0, and $\hat{Q}$ were chosen as example "cases." Then, for each set, runs of computation were performed for specific values of θ_X and θ_M.

Table 1 shows the values of the kinetic parameters for the four example cases that were modeled. Each case corresponds to a fixed set of K_D, Φ_0, and $\hat{Q}$ values where the mixing parameters θ_X and θ_M were varied. Columns 5 and 6 of Table 1 show $(DP_n)_i$ and $(Z_p)_i$, which are the values of DP_n and Z_p for ideal mixing at the end of the batch time (θ_B). They are given as the base-level values that describe the polymer that would be made under ideal mixing conditions for each case.

Table 3. Sample Results for Case 2

θ_X	θ_M	DP_n	Z_p	X_m
0	0	51.6	3.9	1.0
0.1	0.1	51.6	8.7	1.0
1.0	1.0	51.6	45.8	1.0
5.0	5.0	51.6	137.8	1.0
10.0	10.0	51.6	189.0	1.0
0.1	10.0	51.6	4.1	1.0
10.0	0.1	51.5	22.8	1.0

Table 4. Sample Results for Case 3

θ_X	θ_M	DP_n	Z_p	X_m
0	0	24.8	2.2	0.99
0.1	0.1	24.8	2.7	0.99
1.0	1.0	24.7	7.1	0.99
5.0	5.0	24.7	23.2	0.99
10.0	10.0	24.6	39.5	0.99
0.1	10.0	24.8	2.2	0.99
10.0	0.1	24.8	4.2	0.99

Tables 2-5 show some sample results for DP_n, Z_p, and X_m, monomer conversion, at the end of the batch time (500) for cases 1-4, respectively. Each row in Tables 2-5 corresponds to a subcase for the given values of θ_X and θ_M. Note that the first row in each table corresponds to mixing time constants equal to zero, that is, the ideal mixing subcase which is obtained by the solution of Eq. 52. Results in Tables 2-5 are the final values (at the end of θ_B) of DP_n, polydispersity Z_p, and monomer conversion X_m as θ_X and θ_M varied from 0 to 10. In the following discussion of the results of the four cases, no attempt will be made to explain the reasons for various trends observed. It is simply not possible to explain, even qualitatively, all the results from simultaneous solution of the model equations representing all three zones. Instead, significant trends will be pointed out without any bias about the validity of the model which must still be developed by fitting the time constants to experimental data.

Note in Table 2 (case 1) that the final DP_n varies only in the third significant digit with the mixing parameters, while Z_p varies twentyfold from ideal mixing to the highest level of the two mixing parameters, 10 and 10. Similar results, also observed for cases 2-4 in Tables 3-5, mean that the final accumulative value of the number-average degree of polymerization DP_n at nearly complete conversion of the monomer, according to this model, is practically insensitive to mixing, while the weight-average DP_w is quite sensitive to it. Also, the fact that DP_n varies very little while DP_w varies greatly indicates that many very short chains and a few very long chains must be made as a result of imperfect mixing. This is concluded when one considers the definition of the moments of the MWD (Eq. 26) and the relationship between the moments and DP_n and DP_w (Eqs. 31 and 32). This result is quite reasonable for the present model in terms of the partially segregated feed zones in the reaction vessel. It is easy to understand that many short chains can be made in the initiator feed zone while a few very long ones would be made in the monomer feed zone when

Table 5. Sample Results for Case 4

θ_X	θ_M	DP_n	Z_p	X_m
0	0	50.0	4.0	1.0
0.1	0.1	50.0	4.5	1.0
1.0	1.0	49.9	9.3	1.0
5.0	5.0	49.9	29.0	1.0
10.0	10.0	49.9	48.9	1.0
0.1	10.0	50.0	4.3	1.0
10.0	0.1	50.0	6.0	1.0

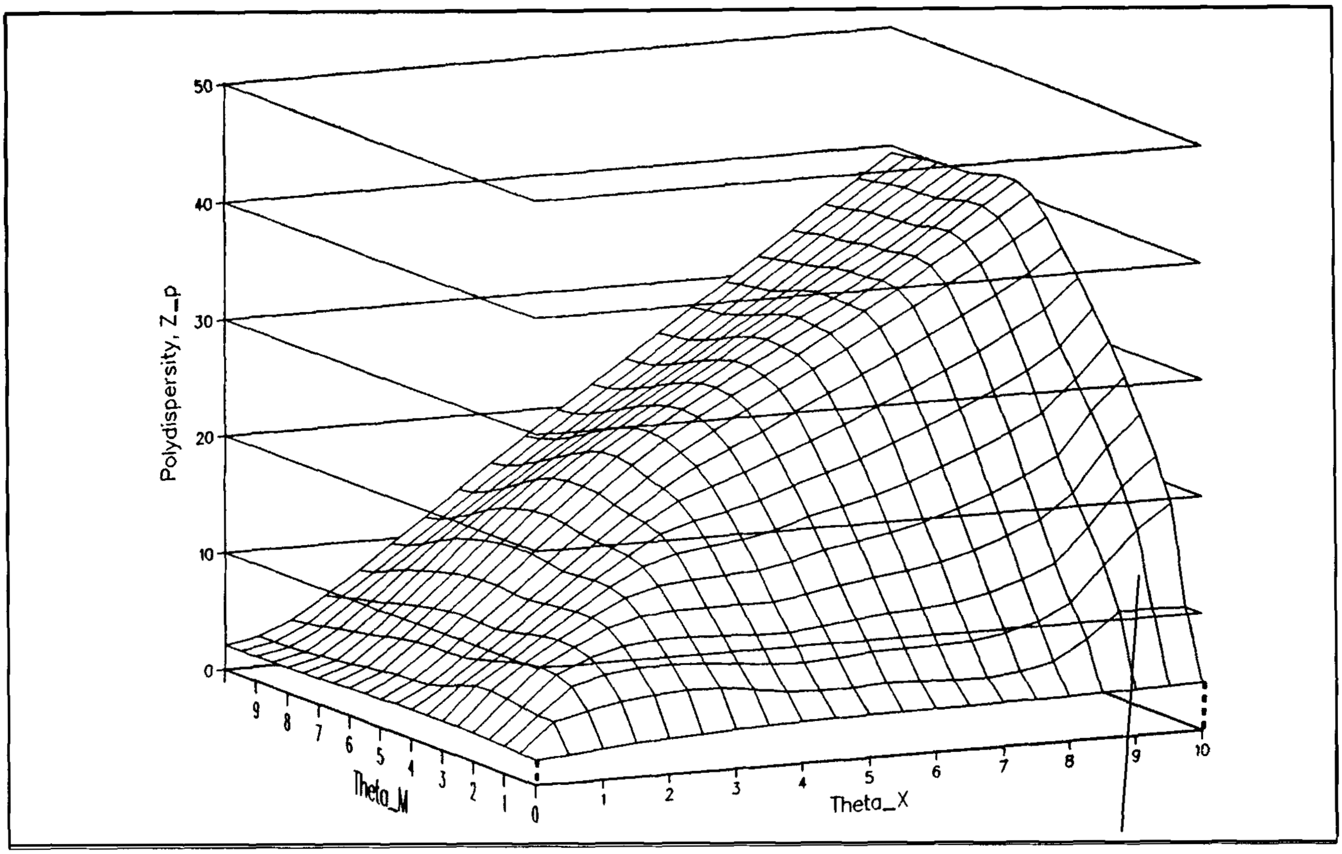

Figure 2. Three-dimensional plot of calculated polydispersity Z_p vs. model parameters θ_M and θ_X for case 1.

one remembers that kinetic chain length, that is the instantaneous number average degree of polymerization for the dead polymer chains being produced, is given by:

$$v = \frac{k_p M}{2(fk_d k_t I)^{1/2}} \tag{57}$$

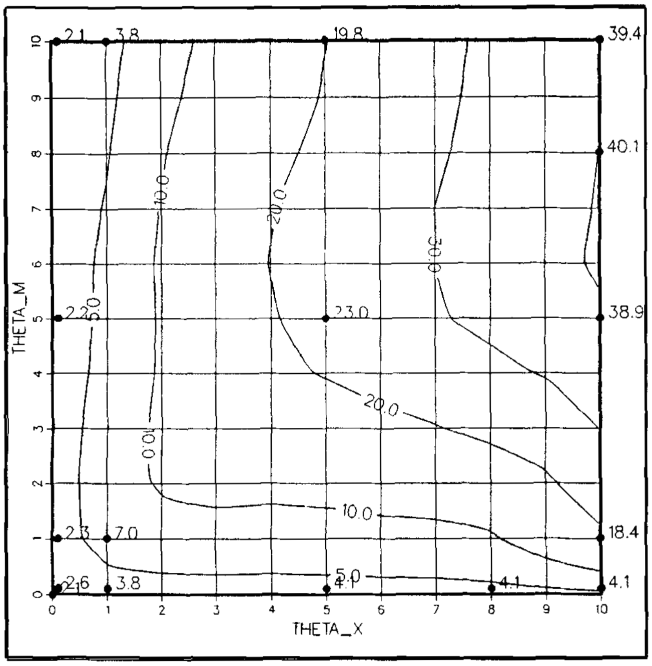

Figure 3. Contour plot of calculated polydispersity Z_p vs. θ_M and θ_X for case 1 (cf. Figure 2).

Figure 2 is a 3-D plot of Z_p vs. θ_X and θ_M for case 1. An interpolation routine was applied to all the model results, some of which are shown in Table 2, to calculate the Z_p surface in Figure 2. Figure 3 shows a two-dimensional contour plot for case 1. Note that the sharpest rise in Z_p appears to be approximately along the diagonal of the plot, that is, at approximately equal values of θ_X and θ_M.

Figures 4-6 show for case 1, plots of DP_n and DP_w vs. dimensionless time for three levels of mixing parameters: $\theta_X = \theta_M = 0$, 0.1, and 10.0, respectively. These plots show accumulative values of DP_n and DP_w as functions of dimensionless time θ. Even though DP_n vs. θ curves look much the same for all three subcases, the sharp spike in DP_w in the two nonideal mixing cases very early in the run (Figures 5 and 6; note logarithmic scale of DP in the latter) distinguishes these cases from the ideal case (Figure 4). It is interesting that even a rather mildly nonideal mixing situation, where the dimensionless mixing time constants are equal to just 0.1 (Figure 5), gives rise to a sharp spike in DP_w, whereas the ideal mixing case shows no such spike. Also, it is worth noting that even though the DP_n curves for the three subcases show no significant difference on the time scale of Figures 4-6, inspection of the numerical values of DP_n over the initial 100 time units (not given here) indicated marked differences between the first two subcases and the third one, while the former (being ideal

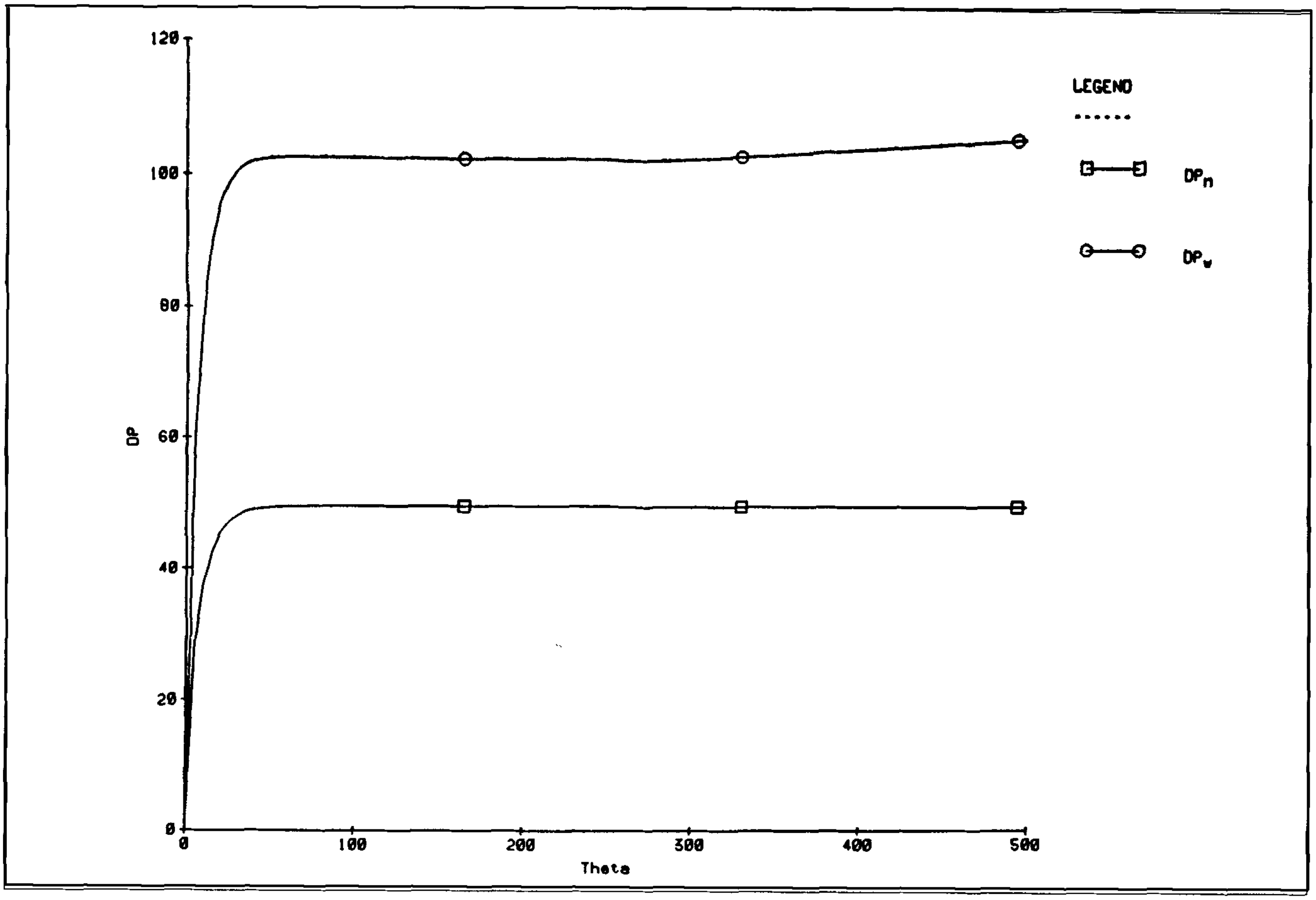

Figure 4. Calculated DP_n and DP_w vs. θ for ideal mixing conditions in case 1: $\theta_M = \theta_X = 0$.

and very nearly ideal) have virtually identical DP_n values throughout the time span.

Table 3 shows sample results for case 2 which differed from case 1 in the value of K_D being equal to 0.010, instead of 0.100. Figure 7 shows a 3-D plot of all the model results for case 2. Comparison of Tables 2 and 3 and Figures 2 and 7 indicates that the values of DP_n varied little with the tenfold change in the value of K_D, while the results for Z_p display great sensitivity to this parameter. This can be concluded by observing that DP_n is about 49.5 for case 1 and about 51.6 for case 2 (over the entire range of time constants), while Z_p varies from 2.1 to 39.4 for case 1 and from 3.9 to a maximum of about 240 (see Figure 7) for case 2 over the range.

Sample results for case 3 in Table 4, on the other hand, show that DP_n is almost directly proportional to Φ_0, while Z_p is virtually unaffected by it over the entire range of mixing variables. This is concluded from comparison of the results in Table 4 with those in Table 2 for case 1, since case 3 differed from case 1 only in the value of Φ_0 (50 vs. 100).

Table 5 shows sample results for case 4 which differed from case 1 in the value of $\hat{Q}$ (0.100 vs. 0.001). Figure 8 shows a 3-D plot of all the model results for case 4. Comparison of Tables 5 and 2 and Figures 8 and 2 shows that DP_n is virtually insensitive to $\hat{Q}$, but variation of Z_p with mixing conditions does show some effect of $\hat{Q}$. Note that in case 4, Z_p varied from 4 to about 50 (twelvefold), while in case 1 it varied from about 2 to about 40 (twentyfold) as the mixing parameters varied from 0 to 10.

Above observations show that according to the present model, variations in mixing intensity from ideal to mildly nonideal and to highly nonideal have little effect on DP_n, but quite strong effects on DP_w. Furthermore, these mixing effects are strongly coupled with variations in the dimensionless initiator rate constant K_D and are somewhat affected by $\hat{Q}$, but are largely independent of the feed concentration ratio Φ_0.

Since the present model is a dimensionless one, no specific values for θ_X and θ_M had to be computed from t_X and t_M, which themselves would have to be determined. For actual cases involving specific kinetic constants and reactor geometry, agitator type, speed, and so on, one must have a method to estimate these parameters. At the present time, there are no generalized correlations available for the time constants of the Villermaux model. However, it is possible to use, as starting estimates, the values of the time constants given by Pohorecki and Baldyga for the mixing model that these workers proposed (1983a,b). Their model is quite similar to the present one by Villermaux (1989) in its assumed mechanisms for the decay of the segregated volume and diffusive mixing with the well mixed bulk. It is proposed that their correlations for t_{md} and t_M be used to estimate t_X and t_M of the Villermaux model. The correlations of Pohorecki and Baldyga (1983b) are:

$$t_{md} = 2.732\,\frac{(D_t/L)(H/L)^{1/2}\,[\ln(Sc) - 1.27]}{(Po)^{1/2}NRe^{1/2}} \tag{58}$$

and

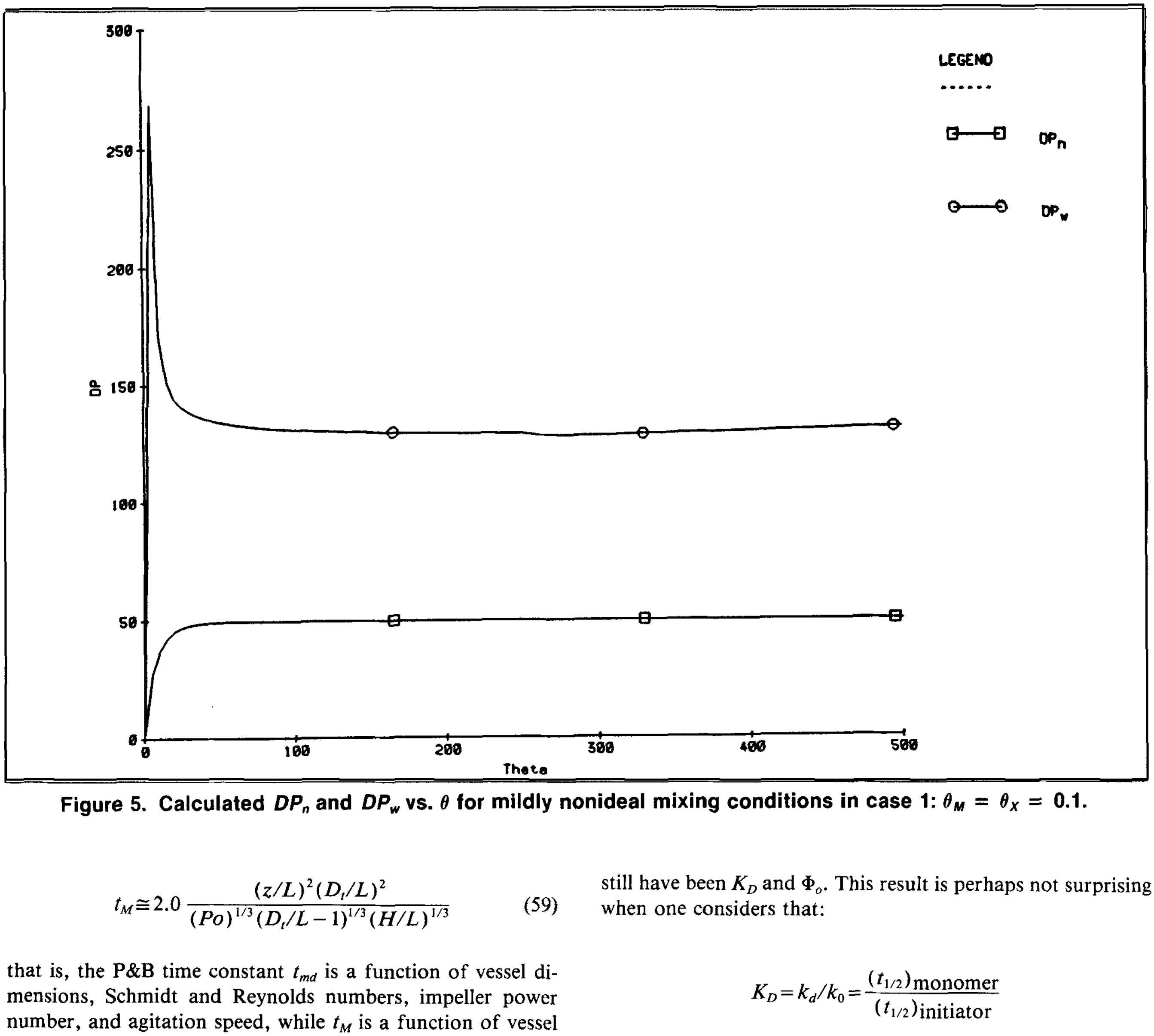

Figure 5. Calculated DP_n and DP_w vs. θ for mildly nonideal mixing conditions in case 1: $\theta_M = \theta_X = 0.1$.

$$t_M \cong 2.0 \frac{(z/L)^2 (D_t/L)^2}{(Po)^{1/3}(D_t/L-1)^{1/3}(H/L)^{1/3}} \tag{59}$$

that is, the P&B time constant t_{md} is a function of vessel dimensions, Schmidt and Reynolds numbers, impeller power number, and agitation speed, while t_M is a function of vessel dimensions, power number, and agitation speed.

If experimental data relating DP_n and DP_w in free radical homopolymerizations to agitation intensity in semibatch stirred-tank reactors were available, it would be possible to check the validity of using the P&B correlations above in the present model by comparing experimental results with the model predictions using the P&B constants. However, no such data are available in the open literature to our knowledge. Another possibility for estimates of t_M and t_X is to follow the recommendation of Villermaux (1989) and use t_c, internal recirculation time, for the former and the eddy lifetime (see earlier discussion) for the latter.

In closing the discussion of results, it must be mentioned that the choice of the reference values used to render the model equations dimensionless is purely arbitrary and another set of reference parameters could just as well have been chosen. For instance, it is interesting to note that if we had defined t_o as $1/k_d$ instead of $1/k_o$ as in Eqs. 44 and 45, then all the dimensionless times and time constants would have been referenced to the half life of the initiator instead of the monomer, but the dimensionless kinetic parameters in the equations would still have been K_D and Φ_o. This result is perhaps not surprising when one considers that:

$$K_D = k_d/k_0 = \frac{(t_{1/2})\text{monomer}}{(t_{1/2})\text{initiator}}$$

that is, K_D is the ratio of rates of initiation and propagation, and that K_D and the dimensionless feed concentration ratio Φ_o together define an intrinsic kinetic chain length v_o for the system as follows:

$$v_0 = \frac{k_p M_o}{(2fk_d k_t I_o)^{1/2}} = \Phi_o / 2fK_D$$

Conclusion

A dimensionless mathematical model of free radical homopolymerization under imperfect mixing conditions in a semibatch stirred-tank reactor has been formulated by combining the "partially segregated feed" model of Villermaux (1989) and a lumped kinetic model based on population balances and moments of the molecular weight distribution. The present model can compute dimensionless concentrations, accumulative number- and weight-average degrees of polymerization, and polydispersity, Z_p as functions of time under ideal or

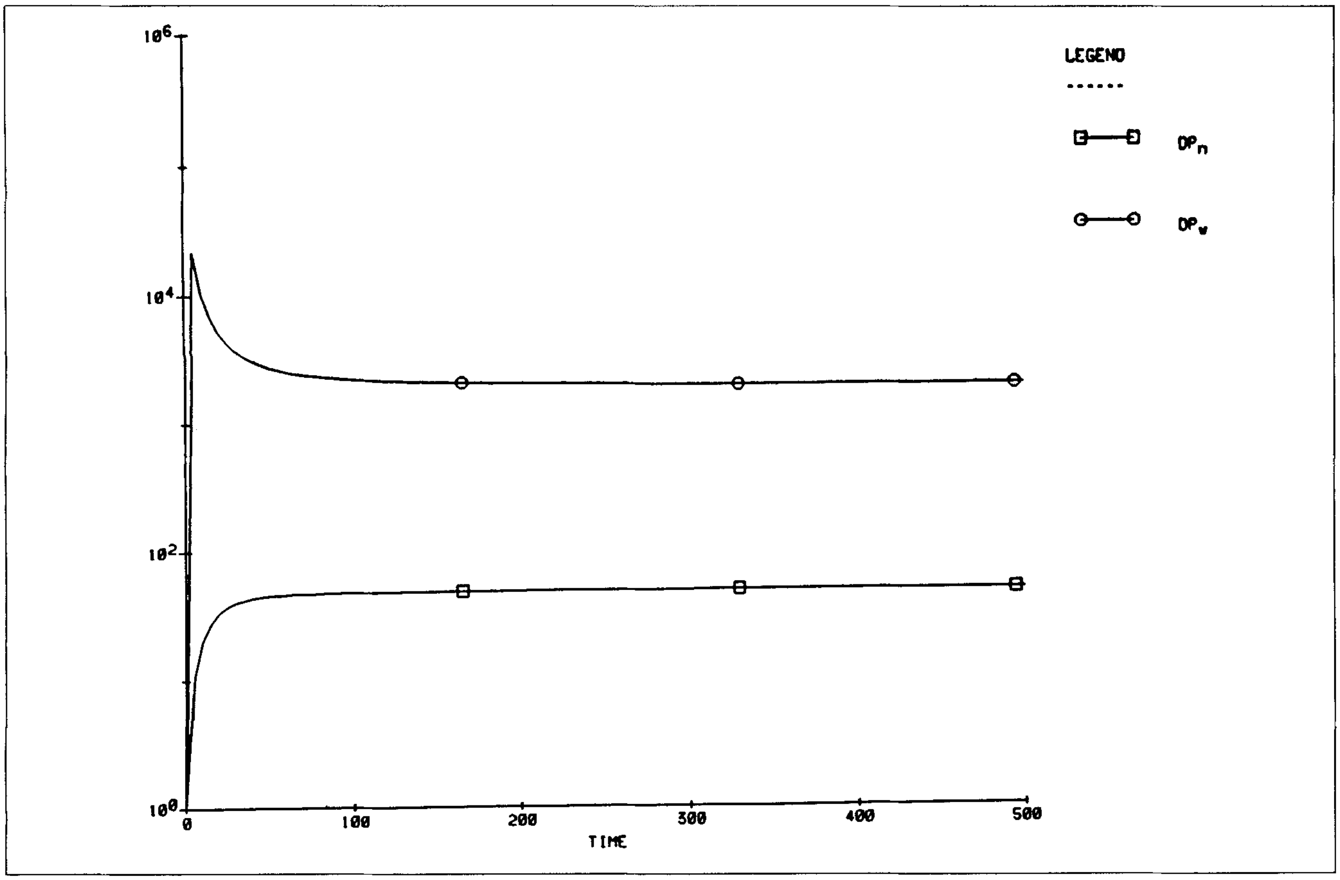

Figure 6. Calculated DP_n and DP_w vs. θ for strongly nonideal mixing conditions in case 1: $\theta_M = \theta_X = 10$.

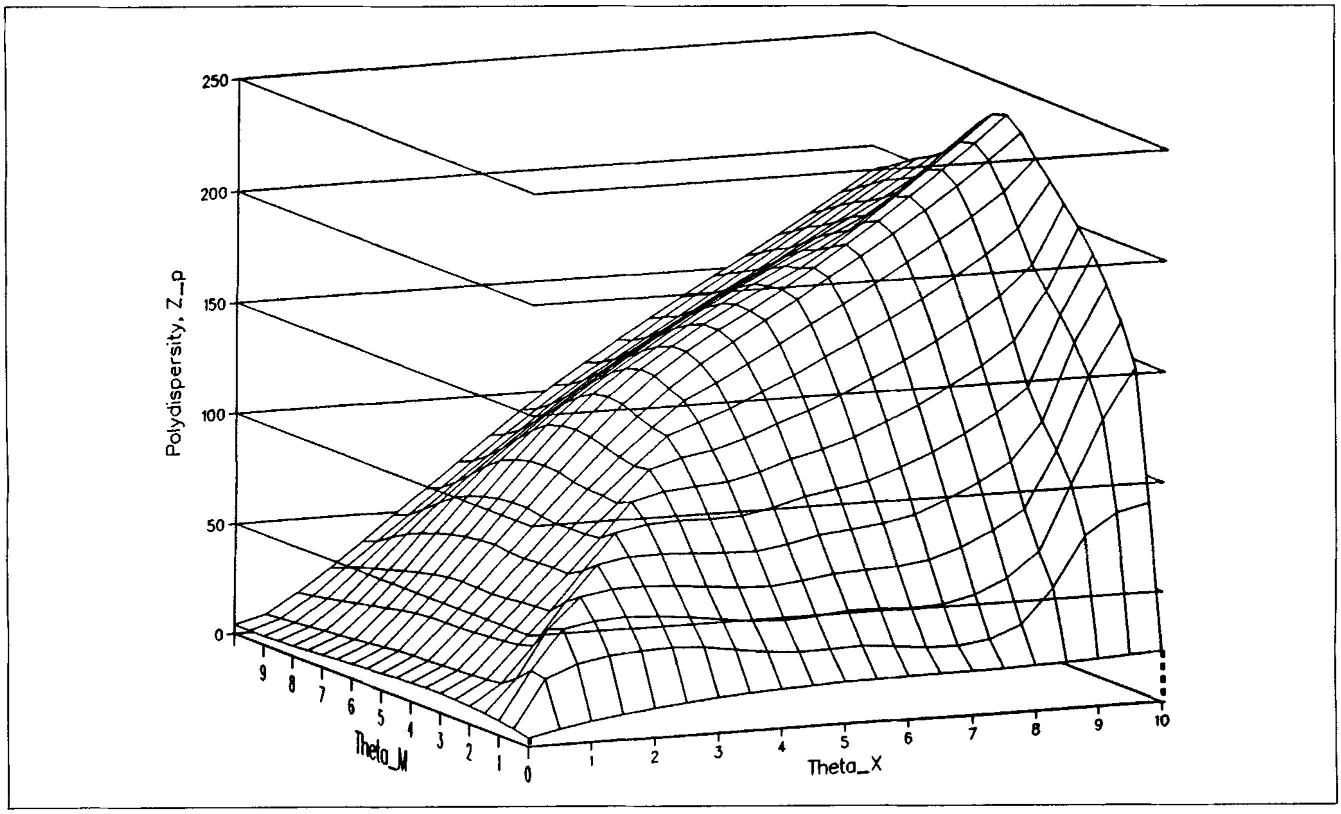

Figure 7. Three-dimensional plot of calculated polydispersity Z_p vs. model parameters θ_M and θ_X for case 2.

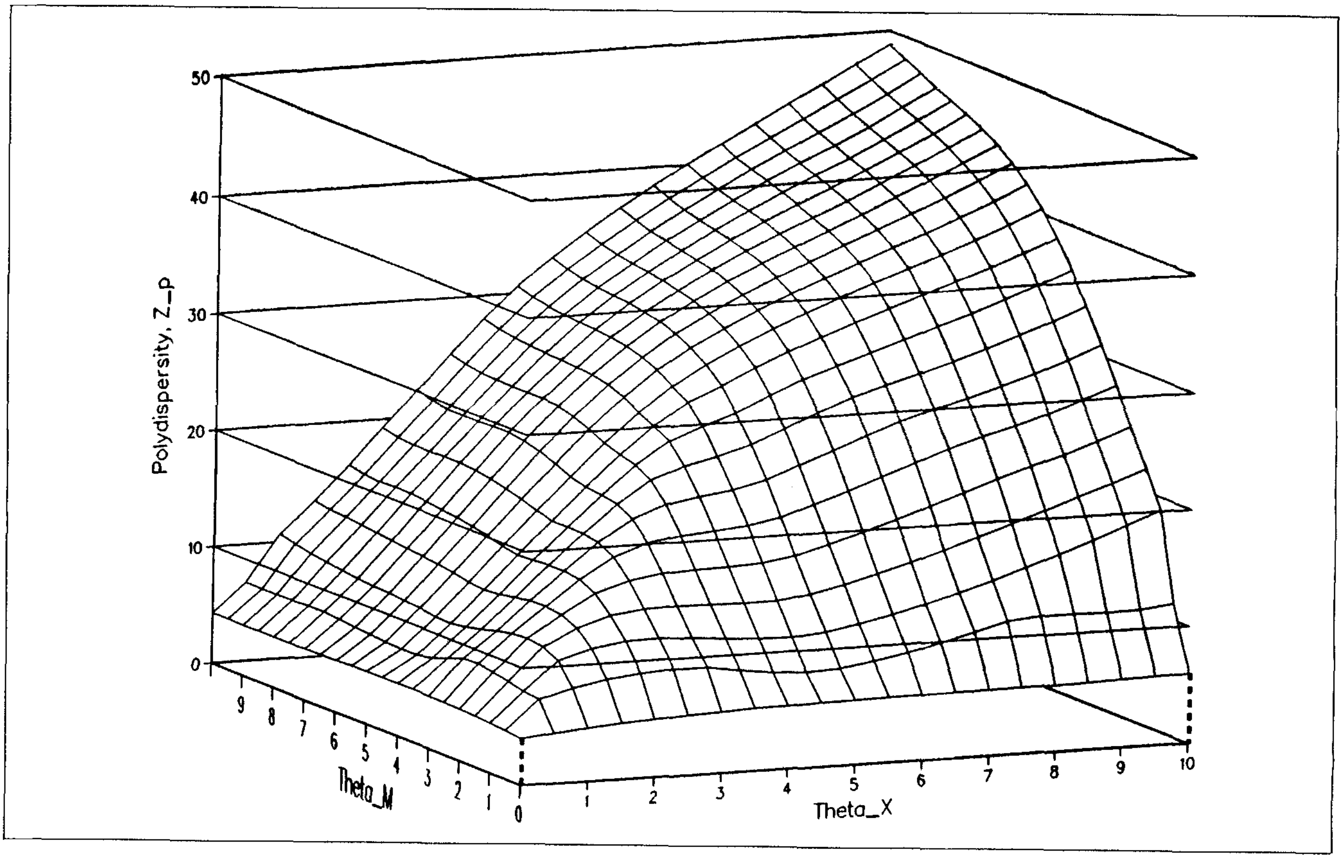

Figure 8. Three-dimensional plot of calculated polydispersity Z_p vs. model parameters θ_M and θ_X for case 4.

nonideal mixing conditions in all three zones. Nonideal mixing conditions are related to dimensionless mixing time constants θ_1, θ_2, and θ_M which can be viewed as Damköhler numbers for micro- and macromixing as defined by the mixing model. As such, the model would be applicable to solution polymerization cases in a semibatch situation where the viscosity is low enough throughout the reaction to permit the assumption of turbulent, well mixed, partially segregated zones of the model and where the viscosity does not vary much so that the approximate constancy of the mixing times can be assumed. However, with appropriate mathematical modifications, the model would also be applicable to melt polymerization in a nonideal, continuous stirred-tank reactor where turbulence is achieved by vigorous agitation and viscosity does not vary at steady state. To our knowledge, such a model has not been available in the open literature up to now.

Since the mixing model used here is given without functional descriptions of its parameters and has yet to be validated, the present polymerization model has been presented as a dimensionless one so that the ratios of the mixing time constants and a characteristic reaction time constant become the dimensionless mixing parameters. As such, it is felt that the present model would be quite helpful in determining tendencies in real systems with respect to the effects of convective and diffusive mixing on polymer MWD in stirred-tank reactors.

At the moment, for dimensional applications only estimates of the mixing times of the model can be used. Generalized correlations for these parameters are needed and the model needs to be validated against experimental data relating product polymer properties to mixing conditions. Such data are not readily available in the literature. It is hoped that the mathematical treatment presented here will encourage work in that direction.

Acknowledgment

The computer code and solution algorithm for the model were prepared by A. Genin. Three-dimensional plots were generated with assistance from C. H. Hales. Discussion of QSSA with G. R. Dalby led to the analysis of the validity of QSSA. The contributions of these individuals are gratefully acknowledged.

Notation

C_j = concentration of species j in ideally mixed reactor
C_{ji} = concentration of species j in volume i
$C_{j1}o$, $C_{j2}o$ = concentrations of species j in feeds
DP_n = number-average degree of polymerization
DP_w = weight-average degree of polymerization
D_t = diameter of reaction vessel
f = initiator effectiveness factor
H = height of liquid in reaction vessel
I_o = concentration of initiator in initiator feed solution
L = turbine diameter
M_o = concentration of monomer in monomer feed solution
N = impeller rotational speed
Po = impeller power number
Q_1, Q_2 = feed flow rates
Re = Reynolds number

R_j = rate of generation of j in ideally mixed reactor by chemical reactions
R_{ji} = rate of generation of species j in volume i by chemical reactions
Sc = Schmidt number
t_1, t_2 = time constants defined by Eqs. 8 and 9
t_{12} = time constant defined by Eq. 10
t_M = time constant defined by Eqs. 1 and 2
V_1, V_2, V_3, V_T = segregated volumes (Figure 1) and total volume
z = function of vessel dimensions defined in P&B (1983b), p. 401
Z_p = polydispersity

Greek letters

λ_k = kth moment of polymer MWD
Φ_o = M_o/I_o
Γ = ratio defined by Eqs. 54-56
θ_1, θ_2, θ_{12} = dimensionless time constants from t_1, t_2
θ_X = shorthand for θ_1 or θ_2
θ_M = dimensionless time constant from t_M
θ_B = dimensionless batch time
θ_F = dimensionless feed time

Special symbol

$\wedge$ = indicator of some dimensionless variables

Literature Cited

Atiqullah, M., and E. B. Nauman, "A Model and Measurement Technique for Micromixing in Copolymerization Reactors," *Chem. Eng. Sci.*, **45**, 1267 (1990).

Baade, W., H. U. Moritz, and K. H. Reichert, "Effects of Mixing and Reactor Type on Polymer Properties," *J. Appl. Polym. Sci.*, **27**, 2249 (1982).

Baldyga, J., and J. R. Bourne, "A Fluid Mechanical Approach to Turbulent Mixing and Chemical Reaction: II. Micromixing in the Light of Turbulence Theory," *Chem. Eng. Commun.*, **28**, 243 (1984).

Chella, R., and J. M. Ottino, "Modeling of Rapidly-Mixed Fast-Cross-Linking Exothermic Polymerizations," *AIChE J.*, **29**, 373 (1983).

Costa, P., and C. Trevissoi, "Some Kinetic and Thermodynamic Features of Reactions between Partially Segregated Fluids," *Chem. Eng. Sci.*, **27**, 653 (1972).

Fields, S. D., and J. M. Ottino, "Effect of Segregation on the Course of Unpremixed Polymerizations," *AIChE J.*, **33**, 959 (1987).

Harada, M., K. Arima, W. Eguchi, and S. Nagata, "Micromixing in a Continuous Flow Reactor (Coalescence and Redispersion Model)," Memoirs of Faculty of Eng., Kyoto Univ., **24**, 431 (1962).

Harada, M., et al., "The Effect of Micromixing on the Homogeneous Polymerization of Styrene in a Continuous Flow Reactor," *J. Chem. Eng. Japan*, **1**, 148 (1968).

Lee, Y.-M., and L. J. Lee, "Effect of Mixing and Reaction on a Fast Step Growth Polymerization," *Int. Polym. Process.*, **1**, 144 (1987).

Marini, L., and C. Georgakis, "The Effect of Imperfect Mixing on Polymer Quality in Low-Density Polyethylene Vessel Reactors," *Chem. Eng. Commun.*, **30**, 361 (1984).

Marini, L., and C. Georgakis, "Low-Density Polyethylene Vessel Reactors," *AIChE J.*, **30**, 401 (1984).

Muhr, H., R. David, and J. Villermaux, "Determination of the State of Micromixing in a Stirred-Tank Reactor by Means of Consecutive-Competitive Reactions and Interpretation of Experimental Data by Different Models," Paper 67f, AIChE Meeting, Chicago (1990).

Murakami, Y., M. Takao, O. Nomoto, and K. Nakayama, "Mixing Effect on Homogeneous Reaction in Batch Stirred-Tank Reactor," *J. Chem. Eng., Japan*, **14**, 196 (1981).

Nauman, E. B., "Mixing in Polymerization Reactors," *J. Macromol. Sci. Revs. Macromol. Chem.*, **C10**, 75 (1974).

Pohorecki, R., and J. Baldyga, "New Model of Micromixing in Chemical Reactors: 1. General Development and Application to a Tubular Reactor," *Ind. Eng. Chem. Fundam.*, **22**, 392 (1983).

Pohorecki, R., and J. Baldyga, "New Model of Micromixing in Chemical Reactors: 2. Application to a Stirred-Tank Reactor," *Ind. Eng. Chem. Fundam.*, **22**, 398 (1983).

Rao, D. P., and L. L. Edwards, "Mixing Effects in Stirred-Tank Reactors: a Comparison of Models," *Chem. Eng. Sci.*, **28**, 1179 (1973).

Ray, W. H., "On the Mathematical Modeling of Polymerization Reactors," *J. Macromol. Sci.-Revs. Macromol. Chem.*, **C8**, 1 (1972).

Tadmor, Z., and J. A. Biesenberger, "Influence of Segregation on Molecular Weight Distribution in Continuous Linear Polymerizations," *I&EC Fundam.*, **3**, 336 (1966).

Thiele, R., and J. Breme, "Micro- and Macromixing in Polymerization Reactors," *Int. Polym. Process.*, **3**, 48 (1988).

Villermaux, J., "A Simple Model for Partial Segregation in a Semibatch Reactor," Paper 114a, AIChE Meeting, San Francisco (1989).

Villermaux, J., and L. Blavier, "Free Radical Polymerization Engineering: I. a New Method for Modeling Free Radical Homogeneous Polymerization Reactions," *Chem. Eng. Sci.*, **39**, 87 (1984).

Villermaux, J., and J. C. Devillon, "Representation de la Coalescence et de la Redispersion des Domaines de Segrégation dans un Fluide par un Modèle d'Interaction Phenomenologique," *Proc. Int. Symp. on Chem. React. Eng.*, Elsevier, Amsterdam, p. B1 (1972).

Manuscript received Aug. 26, 1991, and revision received Dec. 31, 1991.