Influence of Mixing on the Performance of Periodic Chemical Reactors

The interaction between imperfect mixing and cyclic operation is examined for several continuous polymerizations in stirred-tank reactors. The reactor is represented by a mixed model involving two interconnected ideal stirred vessels. Cyclic fluctuations in the concentration of a chain transfer agent during Ziegler-catalyzed olefin polymerization can yield molecular weight distributions significantly different from those of a conventional steady state reactor. This result is consistent with the available experimental data. It is especially interesting that the cyclic reactor effluent with a modified molecular weight distribution is of approximately time-invariant composition when the period of cycling is on the order of the reactor holding time. Imperfect mixing has a lesser effect on cycled reactors for free-radical and polycondensation polymerization than it has on cycled olefin polymerization reactors.

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SCOPE

It is well known that the degree of mixing within a polymerization reactor can significantly affect the product molecular weight distribution (MWD) and thereby the polymer properties. Similarly, intentional unsteady operation of such reactors by varying such operating parameters as feed concentrations or flow rate can produce different MWD's than any steady state operation. This result has been obtained in modeling studies by Ray (1968) for free-radical and polycondensation polymerizations, for example, and demonstrated experimentally by Claybaugh et al. (1969) for Ziegler-catalyzed olefin polymerization. Since commercial reactors may not be perfectly mixed, the objective of this work is to analyze the combined effects of imperfect mixing and cyclic operation.

In this paper a simple model of an imperfectly stirred vessel patterned after that of Manning, Wolf, and Keairns (1965) is employed. The vessel is viewed as two interconnected perfectly mixed regions (see Figure 1). The reaction chosen for major emphasis is Ziegler-catalyzed olefin polymerization since the experimental data of Claybaugh et al. (1969) comes from such a system. The cycled variable is concentration of chain transfer agent, a compound normally added at a steady rate to a polymerization reactor. Such an agent modifies the MWD of the polymer product by deactivating active growing polymer chains [See the reaction mechanism in Equation (1)]. Also, fluctuations in feed monomer concentration to perfectly and imperfectly mixed tank reactors for free-radical and polycondensation polymerizations are investigated via simulation studies.

CONCLUSIONS AND SIGNIFICANCE

Simulation studies of Ziegler-catalyzed olefin polymerization in steady and intentionally cycled continuous flow stirred tank reactors (CSTR) have been conducted. Periodic variation of chain transfer agent concentration can significantly enlarge the choice of available MWD's beyond those attainable from steady state reactor operation. Figure 2 shows results for an imperfectly mixed CSTR and Figure 4 for the perfect mixing cases. In both, the curve marked SS stands for the obtainable MWD under steady state operation, and the line labeled L is the MWD achievable by cycling. Clearly, significantly larger polydispersities may be obtained by cycling. The imperfect mixing model results are in qualitative agreement with the available experimental data of Claybaugh et al. (1969). The perfect mixing model does not pass this test. However, several phenomena neglected in these models may provide alternative interpretations of the available data.

The imperfect mixing model of the Ziegler-catalyzed olefin polymerization also agrees with another experimental finding of Claybaugh et al. (1969): that for certain cycling frequencies a significant broadening in the MWD can be achieved even though the reactor effluent is of uniform time-invariant composition. The simulation results for the imperfectly mixed CSTR are certainly consistent with this finding (see Figure 3). One may conjecture that in such an imperfectly mixed reactor, the reactor serves in a sense as its own surge tank.

Both perfect and imperfect mixing models have also been applied to cycled polycondensation and free-radical polymerization reactors. The results obtained suggest that imperfect mixing is relatively unimportant for these two types of polymerization reactors. It appears that interesting synergistic interaction between mixing and unsteady operation in other cases is most likely to occur for a relatively fast polymerization amenable to large influence by an easily controlled variable such as a photopolymerization.

This paper is a beginning attempt to understand how two phenomena, mixing and unsteady operation, interact to influence chemical reactor behavior. Each of these factors alone is known to affect reactor performance, especially selectivity. Because selectivity is a critical consideration in polymerization reactor design and also due to the availability of some provocative experimental data, polymerization processes will be employed as examples throughout this work.

The degree of mixing can have a profound influence on monomer conversion as well as the molecular weight distribution (MWD) in radiation-induced polymerization (Chen and Hill, 1971, Kawakami and Machi, 1973). Similar effects for photoinitiated chain reactions have been reported by Hill and Felder (1965). In the investigation by Tadmor and Biesenberger (1966), segregation was shown to have a large influence on continuous linear polymerizations. The dependence of the composition distribution of co- and terpolymers on mixing patterns has been revealed by Szabo and Nauman (1969) and Mecklenburgh (1970). Cintron-Cordeno et al. (1968) showed how variations in the velocity profile in a tubular reactor could alter the MWD from continuous polymerizations.

Cyclic operation of polymerization reactors, where one or more process inputs are intentionally varied periodically with time, can significantly enlarge the scope of available MWD's beyond those attainable at steady state. In their studies of perfectly mixed continuous-flow stirred tank reactors (CSTR's), Ray (1968) and Laurence and Vasudevan (1968) showed that periodic variations in monomer or initiator feed concentration could shift the polydispersity significantly from its steady state value for polycondensation, addition polymerization, and free radical polymerization with or without chain transfer to monomer. Banderman (1971) found decreases in polydispersity in his study of a periodic CSTR with a living end polymerization scheme. The patent disclosure of Claybaugh et al. (1969) reports experimental data for cyclic operation of a polypropylene reactor. Besides providing an increase in the polydispersity, periodic variations in the feed concentration of a chain transfer agent produced an approximately uniform product. Later discussion will consider these findings in greater detail.

The combined problem of mixing and unsteady operation has been considered by Nauman (1969, 1973) and Chen (1971). However, their unsteady residence time distribution theories encompass only the extreme cases of maximum mixedness and complete segregation. They have been applied to date only to systems with one or two independent reactions. Rather than attempt to employ their methods for a system with several reactions and complex kinetics, a simple mixed-model (Levenspiel, 1962) of imperfect mixing will be employed here. Besides illustrating qualitative trends, such a simple model can in some instances lend greater conceptual insight than a more complex approach.

SIMPLE MODEL OF AN IMPERFECTLY MIXED CSTR

The model employed in this work, which is shown schematically in Figure 1, is almost identical to that proposed by Manning and co-workers (Manning et al., 1965; Keairns and Manning, 1969). The only distinction is that here the mixing zone is assumed to be perfectly mixed rather than completely segregated. This difference is of little significance for the reaction system of greatest interest here since almost all of the reaction occurs in the reaction zone which receives the feed.

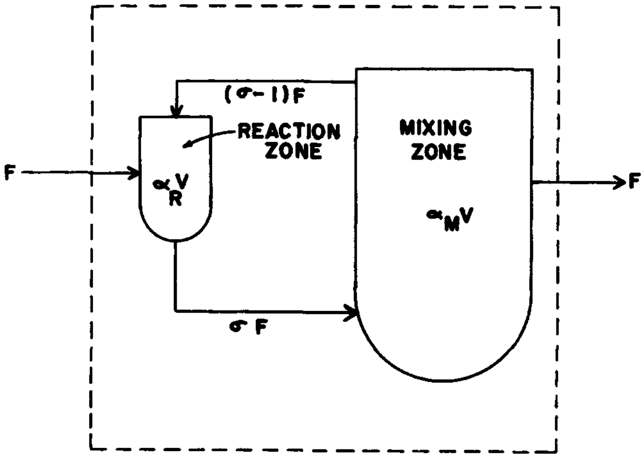

Fig. 1. Schematic diagram of imperfectly mixed CSTR model.

It will be assumed that the reaction and mixing zones are at the same constant temperature. While the latter assumption may be questioned for highly exothermic polymerizations, its use is dictated by the dearth of available kinetic data which precludes accurate estimation of rate constant temperature dependence. Also, utilization of an isothermal model reveals the strong dependence of some polymerization processes on concentration nonuniformities alone. In closing this section it should be noted that experimental realization of precisely the situation shown in Figure 1 has been proposed by Shinnar and Katz (1972) for simulation of small deviations from perfect mixing.

ZIEGLER-CATALYZED OLEFIN POLYMERIZATION

Polymerization of olefins on Ziegler-Natta catalyst has been investigated extensively for the past 15 years. It is known that the Ziegler-Natta catalyst is very active and almost always leads to a polymer with molecular weight too high for processing or fabrication. Schemes for controlling the MWD include the use of hydrogen and other chain transfer agents in the reactor feed stream.

The reactions involved in olefin polymerization by Ziegler-Natta catalyst in the presence of a chain transfer agent are (Natta, 1959; Hoffman et al., 1963; Grieveson, 1965):

Initiation

$$I + M_1 \xrightarrow{k_i} P_1 \tag{1a}$$

Propagation

$$P_n + M_1 \xrightarrow{k_p} P_{n+1} \tag{1b}$$

Termination

$$P_n + M_1 \xrightarrow{k_f} P_1 + M_n \tag{1c}$$

$$P_n + W \xrightarrow{k_s} I + M_n \tag{1d}$$

$$P_n \xrightarrow{k_t} I + M_n \tag{1e}$$

Chain Transfer

$$P_n + H_2 \xrightarrow{k_h} I + M_n \tag{1f}$$

where M_1 is the monomer, P_n is the active polymer with chain length n, M_n is "dead" or unreactive polymer with chain length n, and H_2 is hydrogen, the chain transfer agent. All rates for these reactions are first order in all reactants except the initiation rate (which is zero order with respect to monomer) and the chain transfer reaction rate (which is ½ order with respect to hydrogen concentration). These reactions will be treated here as though they were homogeneous. All local mass transfer processes are therefore ignored, a feature which must not be forgotten when interpreting the simulation results which follow.

The development of a mathematical model for polymerization in a CSTR is begun by defining moment generating functions as in Ray's papers (1967, 1968, 1972)

$$G(s,t) = \sum_{n=1}^{\infty} s^n \, P_n(t) \tag{2}$$

$$H(s,t) = \sum_{n=1}^{\infty} s^n \, [P_n(t) + M_n(t)] \tag{3}$$

and their respective rates of formation

$$r_G = \sum_{n=1}^{\infty} s^n r_{P_n}(t) = s[k_i(I) + k_f(M_1)G(1,t)] - G(s,t) \\ \{(M_1)\,[k_f + (1-s)k_p] + k_s(W) + k_t + k_h(\mathrm{H}_2)^{1/2}\} \tag{4}$$

$$r_H = \sum_{n=1}^{\infty} s^n[r_{P_n}(t) + r_{M_n}(t)] = s\, k_p\, (M_1) \\ [G(s,t) - G(1,t)] - k_p\,(M_1)\, G(s,t) \tag{5}$$

where r_{P_n} and r_{M_n} are, respectively, the rates of formation of live and dead polymers of chain length n. These rates can be easily formulated from the reaction mechanism described above. As will be outlined next, r_G and r_H are important quantities in the final equations for computing all the moments of the MWD.

If pure monomer feed, constant total initiator concentration, constant total feed flow rate and perfect control of hydrogen concentration in the reactor are assumed, then the mass balances for monomer and polymers over the reaction zone are

$$\frac{d(M_1)_R}{dt'} = \frac{1}{\theta}\,[(M_1{}^0)_R - (M_1)_R] + r_{M_1} \tag{6}$$

$$\frac{d(M_n)_R}{dt'} = -\frac{(M_n)_R}{\theta} + r_{M_n} \quad n = 2, 3, \ldots \tag{7}$$

$$\frac{d(P_1)_R}{dt'} = \frac{-(P_1)_R}{\theta} + r_{P_1} \tag{8}$$

$$\frac{d(P_n)_R}{dt'} = \frac{-(P_n)_R}{\theta} + r_{P_n} \quad n = 2, 3, \ldots \tag{9}$$

where, for example, r_{M_1} is the rate of formation of monomer and r_{P_1} is that of active polymer P_1. Multiplying Equations (6), (8) by s and (7), (9) by s^n and adding the resulting equations, the following result is obtained if Equations (3) and (5) are used:

$$\frac{d\,H(s,t')}{dt'} = \frac{1}{\theta}\,[s(M_1{}^0) - H(s,t')] + r_H \tag{10}$$

Similarly, after multiplying Equations (8) by s and (9) by s^n, adding the resulting equations, and then using definitions (2) and (4), the following equation is obtained

$$\frac{d\,G(s,t')}{dt'} = \frac{-G(s,t')}{\theta} + r_G \tag{11}$$

Starting from Equations (6) and (8) and introducing dimensionless variables, Equations (12) and (16) result respectively. Using (10) or (11) and the definitions of ξ_i and z_i (see notation), the remaining reaction zone equations are readily obtained.

Most of the dimensionless variables used below have convenient physical interpretations. For example, y denotes the dimensionless monomer concentration. Also, ξ_0 and ξ_1 are the first two concentration moments: ξ_0 denotes the total concentration of the living and dead polymers in the reactor, and ξ_1 stands for the total amount of monomer units in the living and dead polymers. The variables z_0 and z_1 have meanings corresponding to ξ_0 and ξ_1 but apply to the living polymers only. z_2 and ξ_2 are the second concentration moments defined from $G(s,t)$ and $H(s,t)$, respectively.

Reaction Zone

$$\frac{dy_R}{dt} = \frac{1}{\alpha_R}\,[y^0 - \sigma y_R + (\sigma - 1) y_M] \\ - y_R\,[(k_2 + k_3)z_0 - k_3 p_R] - k_1 \\ + (k_4 u^{1/2} + k_5 + k_6) p_R \tag{12}$$

$$\frac{d\xi_{0R}}{dt} = \frac{1}{\alpha_R}\,[y^0 - \sigma \xi_{0R} + (\sigma - 1)\xi_{0M}] - k_2 y_R z_0 \tag{13}$$

$$\frac{d\xi_{1R}}{dt} = \frac{1}{\alpha_R}\,[y^0 - \sigma \xi_{1R} + (\sigma - 1)\, \xi_{1M}] \tag{14}$$

$$\frac{d\xi_{2R}}{dt} = \frac{1}{\alpha_R}\,[-\sigma \xi_{2R} + (\sigma - 1)\, \xi_{2M}] + 2k_2 y_R z_{1R} \tag{15}$$

Application of the kinetic quasi steady state assumption (QSSA) for active polymers yields

$$p_R = \frac{k_1 + k_3 y_R z_0}{(k_2 + k_3) y_R + k_4 u^{1/2} + k_5 + k_6} \tag{16}$$

$$z_0 = \frac{k_1}{k_4 u^{1/2} + k_5 + k_6} \tag{17}$$

$$z_{1R} = \frac{k_1 + (k_2 + k_3) y_R z_0}{k_3 y_R + k_4 u^{1/2} + k_5 + k_6} \tag{18}$$

Similarly, mass balances for monomer and polymer over the mixing zone and subsequent mathematical manipulation leads to the following equations:

Mixing Zone

$$\frac{dy_M}{dt} = \frac{\sigma}{\alpha_M}\,(y_R - y_M) - y_M\,[(k_2 + k_3)z_0 - k_3 p_M] \\ - k_1 + (k_4 u^{1/2} + k_5 + k_6) p_M \tag{19}$$

$$\frac{d\xi_{0M}}{dt} = \frac{\sigma}{\alpha_M}\,(\xi_{0R} - \xi_{0M}) - k_2 y_M z_0 \tag{20}$$

$$\frac{d\xi_{1M}}{dt} = \frac{\sigma}{\alpha_M}\,(\xi_{1R} - \xi_{1M}) \tag{21}$$

$$\frac{d\xi_{2M}}{dt} = \frac{\sigma}{\alpha_M}\,(\xi_{2R} - \xi_{2M}) + 2k_2 y_M z_{1M} \tag{22}$$

with

$$p_M = \frac{k_1 + k_3 y_M z_0}{(k_2 + k_3) y_M + k_4 u^{1/2} + k_5 + k_6} \tag{23}$$

and

$$z_{1M} = \frac{k_1 + (k_2 + k_3) y_M z_0}{k_3 y_M + k_4 u^{1/2} + k_5 + k_6} \qquad (24)$$

Following Denbigh (1947), the number-average molecular weight μ_1 and the weight-average molecular weight μ_2 are defined by and can be computed from the following equations:

$$\mu_1 = \left(\frac{\sum_{n=2}^{\infty} nM_n + \sum_{n=1}^{\infty} n\,P_n}{\sum_{n=2}^{\infty} M_n + \sum_{n=1}^{\infty} P_n} \right) \cdot MW$$

$$= \left(\frac{\xi_1 - y}{\xi_0 - y} \right) \cdot MW \qquad (25)$$

$$\mu_2 = \left(\frac{\sum_{n=2}^{\infty} n^2 M_n + \sum_{n=1}^{\infty} n^2 P_n}{\sum_{n=2}^{\infty} nM_n + \sum_{n=1}^{\infty} n\,P_n} \right) \cdot MW$$

$$= \left(1 + \frac{\xi_2}{\xi_0 - y} \right) \cdot MW \qquad (26)$$

The control variable u in the above equations is the dimensionless concentration of chain-transfer agent. It is implicitly assumed that this concentration can be manipulated at will within the limits $u_{\min}$ and $u_{\max}$:

$$u_{\min} \leqq u \leqq u_{\max} \qquad (27)$$

This idealization is analogous to those used in other studies of periodic reactors (see Bailey, 1973) and is intended to reveal the maximum influence that cycling of feed chain-transfer agent concentration can have on the polymer MWD.

For steady state operation of the polymerization reactor, u assumes a time-invariant value satisfying restriction (27). Only the class of bang-bang periodic controls will be considered here since this type of control has proved the most interesting in many instances (see Bailey, 1973). Thus for the periodic case,

$$u(t) = \begin{cases} u_{\min} & 0 \leqq t < \gamma\tau \\ u_{\max} & \gamma\tau \leqq t < \tau \end{cases} \qquad (28)$$

and

$$u(t) = u(t + \tau), \quad t \geqq 0 \qquad (29)$$

where τ is the period for the cyclic operation. The reactor attains a periodic state when all of the concentrations are periodic functions. This provides boundary conditions for all of the variables above, which, using y_M as an example, may be written

$$y_M(t) = y_M(t + \tau); \quad t \geqq 0 \qquad (30)$$

The time-average values of number-average molecular weight ($\bar{\mu}_1$), weight-average molecular weight (μ_2) and polydispersity ($\bar{\mu}_2/\bar{\mu}_1$) of the effluent polymers can be computed using

$$\bar{\mu}_1 = \left(\frac{\bar{\xi}_{1M} - \bar{y}_M}{\bar{\xi}_{0M} - \bar{y}_M} \right) \cdot MW \qquad (31)$$

$$\bar{\mu}_2 = \left[1 + \left(\frac{\bar{\xi}_{2M}}{\bar{\xi}_{1M} - \bar{y}_M} \right) \right] \cdot MW \qquad (32)$$

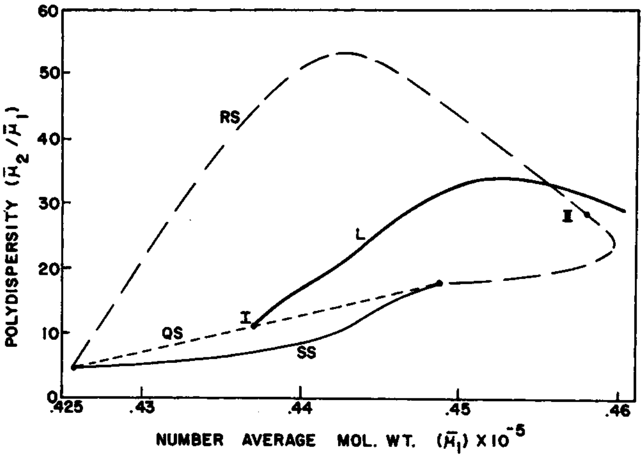

Fig. 2. Number average molecular weights and polydispersities attainable by steady state (SS) and slow (QS), fast (RS), and intermediate (L) cyclic operation.

where an overbar denotes time-averaging over the period, for example,

$$\bar{y}_M = \frac{1}{\tau} \int_0^{\tau} y_M(t)\, dt \qquad (33)$$

REACTOR BEHAVIOR UNDER STEADY STATE AND PERIODIC OPERATION

The various values of number-average molecular weight and polydispersity which can be obtained in steady state operation of the polymerization reactor are shown in Figure 2 by the curve SS. Each different point on the curve corresponds to a different steady concentration of chain transfer agent. The kinetic and reactor parameters employed in the calculations leading to Figure 2 are listed next. The rate constants were chosen so that batch ethylene polymerization simulations gave results in approximate agreement with the available experimental data (Grieveson, 1965), while the reactor design parameters were taken from the Claybaugh et al. patent (1969) whenever possible. Although the value of σ, the recirculation ratio, depends solely upon the pumping capacity of the impeller, the choice of α_R and α_M values is related to the effective volume of the impeller. All these values can in principle be determined experimentally (Manning et al., 1965) although no such mixing data is available from Claybaugh et al. Consequently the values of parameters α_R, α_M, and σ were chosen to achieve the best fit to the available experimental kinetic data. The resulting $\bar{\mu}_1$ and $\bar{\mu}_2/\bar{\mu}_1$ values which were obtained are within the range of values reported by other investigators for this type of reaction (Claybaugh et al., 1969; Boor, 1967; Grieveson, 1965).

$$\theta(\text{hr}) = 2, \quad I(\text{mole/l}) = 0.525 \times 10^{-3}, \quad M_1^0\ (\text{mole/l}) = 0.52 \times 10^{-2}$$

$$y^0 = 1, \quad MW(\text{ethylene}) = 28$$

$$k_1 = 0.630 \times 10^{-3}, \quad k_2 = 0.624 \times 10^{7}, \quad k_3 = 0.624$$

$$k_4 = 0.865 \times 10^{3}, \quad k_5 + k_6 = 0.120 \times 10^{2}$$

$$\alpha_R = 0.1, \quad \alpha_M = 0.9, \quad \sigma = 2$$

$$u_{\min} = 0, \quad u_{\max} = 0.1, \quad \gamma = 0.5$$

In the investigation of periodic reactor behavior, it is reasonable to first examine the limits of very slow (quasi-steady) cycling and very fast (relaxed steady) cycling.

For relaxed steady cycling, the system variables cannot follow the rapid input variations and are approximately time-invariant. In the opposite extreme, quasi steady cycling, the input and the reactor output are related at each instant as they are in steady state. The calculation of system performance for these limiting cases can be accomplished relatively simply using standard techniques (see Horn and Bailey, 1968; Bailey and Horn, 1970; Bailey, 1973). It is necessary only to solve algebraic equations for these situations; lengthy numerical solution of the governing differential equations is avoided. Moreover, the reactor performance for intermediate cycling periods is often bounded between the quasi-steady and relaxed-steady extremes.

The curves labeled QS and RS in Figure 2 show the possibilities for quasi steady and relaxed steady periodic operations, respectively. The parameter which varies along each curve is γ, the fraction of the period in which the minimum chain transfer agent concentration is used. It is clear that cyclic operations can greatly expand the class of available molecular weight distributions far beyond those obtainable under convention steady state design of the polymerization reactor.

Practical considerations dictate, however, that neither the relaxed nor quasi steady extremes are of great interest. As in other studies of cyclic reaction systems (see Bailey and Horn, 1969, 1972; Bailey et al., 1971; Bailey, 1973), success of relaxed steady periodic control also means that the mathematical process model is oversimplified. If an input variable to a real physical process is cycled more and more rapidly, the influence of its variations will in most cases eventually disappear. In the present instance, the addition of a material balance for the chain transfer agent and inclusion of mass transfer resistance in the reactor model would eliminate the effect of very fast cycling. Presumably such a refinement would also limit the maximum attainable dispersity to values smaller than those achieved with the idealized model.

Still, it is known that analysis of an idealized process model in the relaxed steady limit often provides a correct qualitative prediction of the influence of cycling on the process. This is the intent of the present study. Comparison with available experimental results shows that here too the qualitative trends are properly anticipated. In the experimental data revealed in the Claybaugh et al. patent (1969), steady addition of hydrogen to a propylene polymerization reactor yields a product with a polydispersity of 8.0, while a polydispersity value of 10.8 was obtained when the hydrogen addition rate was varied periodically. The model results just reviewed show the same trend.

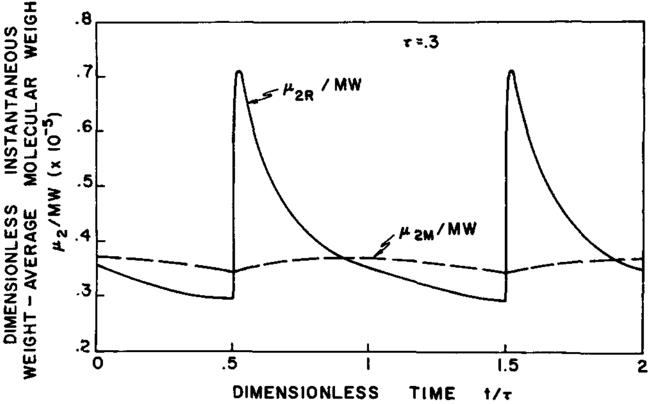

Fig. 3. The instantaneous behavior of the weight average molecular weight in the reaction zone (μ_{2R}/MW) and reactor effluent (μ_{2M}/MW).

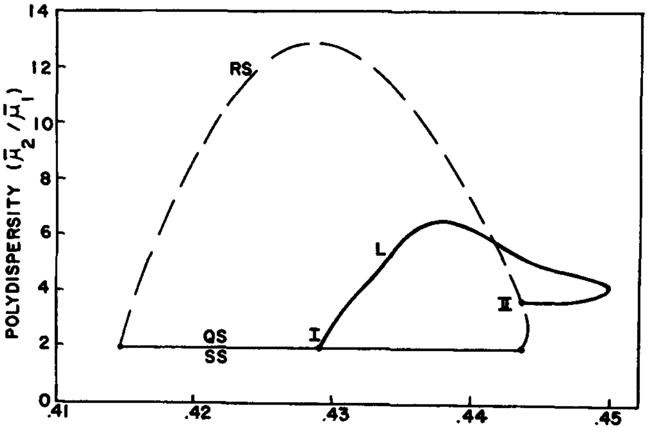

Fig. 4. Performance of a perfectly mixed polymerization CSTR.

Quasi steady periodic operation suffers from the practical disadvantage of large fluctuations in output product composition. Therefore, if the cyclic reactor is to be interfaced with a steady state plant, a surge tank must be installed to damp the periodic reactor effluent. For polymers this is not a simple operation, since "it requires blending and extrusion equipment and personnel, necessitates considerable additional product testing, and additional extrusions of the mixed polymer may be required in order to insure the utmost homogeneity in the product for uses such as polypropylene film" (Claybaugh et al., 1969).

When examining the behavior of the model reactor at frequencies between the two extremes just discussed, an extremely interesting result from the Claybaugh et al. patent (1969) related to these blending difficulties should be considered. It was found experimentally that for certain frequencies, a significant broadening in the MWD could be achieved even though the reactor effluent was of uniform, time-invariant composition and no subsequent blending was required. The dimensionless period τ for experimental realization of the phenomenon was approximately 0.30. Simulation using the above model with this period and $\gamma = 0.5$ gives $\bar{\mu}_2/\bar{\mu}_1 = 22.7$. This is 29% larger than the maximal polydispersity which can be achieved in steady state operations.

Moreover, the instantaneous effluent polymer composition obtained in this simulation was almost time-invariant as can be seen in Figure 3. There the periodic fluctuations in μ_2, the weight-average molecular weight, are shown for both the reaction zone μ_{2R} and the mixing zone μ_{2M}. While very large fluctuations are observed in the reaction zone, the mixing zone (= effluent) material exhibits behavior quite consistent with the experimental findings of Claybaugh et al. (1969). One may conjecture that in such an imperfectly mixed reactor the reactor serves in a sense as its own surge tank.

The objective in the following sections is to explore the extension of the concept to other types of reactions and also to investigate interaction between cycling and mixing for these systems.

Before examining other types of polymerizations, however, there are several additional features of the present system worthy of note. The line labeled L in Figure 2 was obtained by simulating periodic operation of the imperfectly mixed olefin polymerizer over a range of peri-

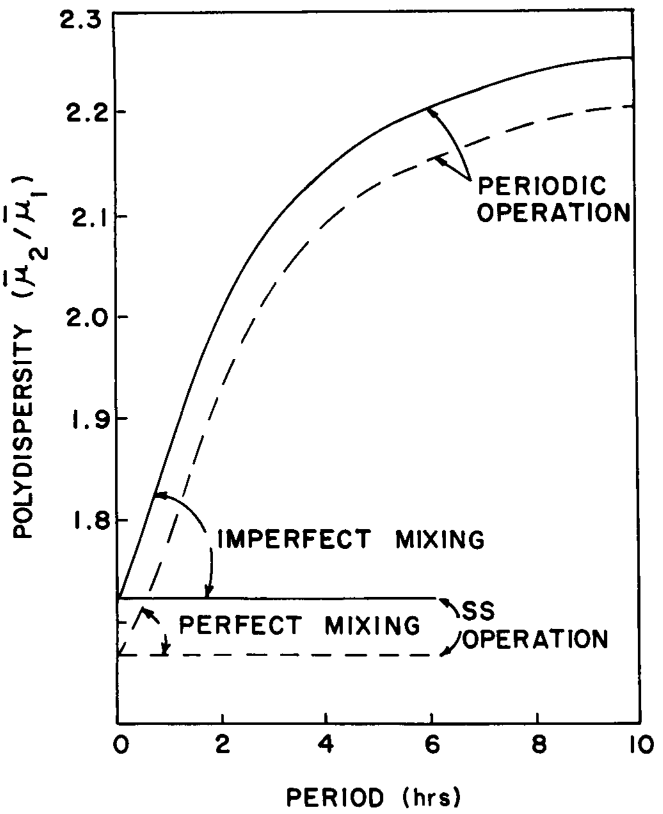

Fig. 5. The influence of cycling period τ and imperfect mixinng on polydispersities for free radical polymerization in a CSTR.

ods from $\tau = 20$ to $\tau = 0.01$ with γ fixed at ½. In computing the periodic solutions of the system Equations (12) to (24) with periodic control (28) and (29), the Runge-Kutta integration scheme was used. When the periodicity conditions, Equation (30) for example, for all of the variables were reached with sufficiently small error, the periodic system variable solutions were used to compute the necessary time-averaged quantities. Prohibitive computing requirements precluded calculations for smaller periods. The dimensionless period τ varies from very large values in the neighborhood of point I on the quasi steady line to small values at the right-hand end point of line L. Point II is the relaxed steady asymptotic result. The novel feature seen in Figure 2 is the escape of line L from the region enclosed by the SS and RS curves. This means that even for this idealized system where relaxed steady periodic operation is of obvious value, an intermediate period will be optimal for certain situations. Such behavior has not been observed before for periodic reaction systems.

The influence of imperfect mixing on both the steady state and periodic performance of the present reaction system may be seen by comparing Figures 2 and 4. Figure 4 shows the sets of number-average molecular weights and polydispersities which are realizable in a single perfectly mixed CSTR. As in the previous figures, the curves marked SS, QS, RS, and L correspond to steady state, quasi steady periodic, relaxed steady periodic, and intermediate periodic operation, respectively. Again L escapes from the region enclosed by the QS and RS plots. However, the polydispersity values obtained for this case are too small relative to the reported range of values obtained experimentally. Lengthy numerical experimentation with other possible kinetic parameters did not rectify this situation. Consequently the perfect mixing, pseudo homogeneous reaction model is not adequate for modeling the Ziegler-catalyzed polymerization of olefins. There are, however, other modeling approaches which yield polydispersities in the proper range. One of these (Schmeal and Street, 1972) considers mass transfer within the expanding polymer-catalyst globule. This was not considered here because it complicates the model considerably and detracts from the major concern of mixing effects.

INVESTIGATIONS OF OTHER TYPES OF POLYMERIZATION

Free-radical polymerization with chain transfer in both cycled imperfectly mixed and ideal CSTR's has been investigated. The dimensionless material balances for the imperfect mixing case are a straightforward extension of the equations presented by Ray (1969). Also, the same kinetic parameters were used here as in Ray's study (1969). Figure 5 shows the effect of cycling feed monomer concentration y^0 between the values $y^0_{\max}$ and $y^0_{\min}$ using a bang-bang control form exactly analogous to that given in Equations (28) and (29). The overall residence time V/F used for these simulations was 7.5 hours. For both steady state and cyclic operation, the influence of imperfect mixing is much less critical than for the previous mechanism.

It may be of interest to draw a rough analogy between the influence of mixing in the steady state and the cyclic reactor results. When mixing is poor, from the standpoint of the present model a fluid element will pass back and forth between two regions of different reaction conditions; that is, the conditions in the reaction and mixing regions, in its sojourn from the reactor inlet to the outlet. Thus, from a Lagrangian point of view, such a fluid element undergoes time variations in its operating conditions. In a rough sense the fluid particle encounters a cycle in space which may be related in an approximate way to the cycles in time encountered in cyclic operation. Consequently the influence of imperfect mixing is the same qualitatively as the cycling effect: an increase in the polydispersity results. Such space-time analogies have been noted before for periodic systems (see Bailey, 1973; Kawakami and Machi, 1973).

Both perfectly and imperfectly mixed models of polycondensation reactors with feed monomer concentration cycling have been investigated. Here too the mixing effect was not of great interest. The periodic performance for the imperfectly-mixed system was very similar to the findings of Ray (1969) for the ideal CSTR case.

DISCUSSION

While the imperfect mixing model employed in this work does yield results consistent with the available data for olefin polymerization on Ziegler-Natta catalyst, it must be recognized that many of the complexities of this heterogeneously catalyzed reaction system have been ignored here. The influence of local mass transfer to an expanding catalyst particle has been ignored (Schmeal and Street, 1971), as have possible heterogeneities in catalyst particle activity (Keii, Soga, and Saika, 1967). The interactions of composition and reaction rates with the temperature and viscosity of the reaction mixture have also been neglected in this investigation.

Perhaps more serious, the model for imperfect mixing used here is one that does not explicitly consider the inherent segregation which must occur in the case of a heterogeneously catalyzed polymerization in solution. It certainly cannot be asserted that the segregation effects ignored in this analysis are not important. The assumption of complete segregation for all components does not, however, seem reasonable for this system since the catalyst-polymer globules of various ages are in communication via the monomer species in solution. No analytical methods for such a system appear to be available at present, and their development seems a worthwhile goal for future research. As stated earlier, the model for imperfect mixing used here was chosen because it allows a starting look at mixing effects in complex periodic systems without the necessity for extremely lengthy mathematical or computational analysis. Also, the present model permits straightforward interpretation of the internal surge tank and cycle in space concepts which may find more general applicability in chemical reaction engineering.

The results for the free-radical and polycondensation cases show that the large influences of mixing and cycling found in the Ziegler-catalyzed polymerization are not universal. In this context it may be worthwhile to point out the major differences among these reaction systems. First, the Ziegler-catalyzed olefin polymerization is a relatively fast reaction, with 90% conversion of monomer being reached in the small reaction zone. For the other cases there is a significant amount of reaction in the so-called "mixing region" so the overall system behaves more like a single ideal CSTR. Also, in the olefin polymerization a very strong control of the reaction process, namely the amount of chain-transfer agent feed to the reactor, is available. The feed monomer fluctuations employed for the other reactors have a relatively small influence on the process. From these observations one may speculate that the interactions between cycling and mixing may be of interest in photopolymerization, which are also relatively fast and which are amenable to large influence under an easily controlled variable, namely the irradiation intensity. Extensions to copolymerizations on Ziegler-Natta catalysts are possible as discussed in the Claybaugh et al. patent (1969). Modeling studies of these systems is also an inviting area for further work.

NOTATION

F = feed flow rate
$G(s, t)$ = moment generating function, see Equation (2)
$H(s, t)$ = moment generating function, see Equation (3)
H_2 = hydrogen
(H_2) = hydrogen concentration
I = initiator
(I) = initiator concentration
k_i = initiation rate constant
k_p = propagation rate constant
k_f, k_s, k_t = termination rate constants
k_h = chain transfer rate constant
k_1 = dimensionless rate constant, = $k_i\theta(I)/(M_1^0)$
k_2 = dimensionless rate constant, = $k_p\theta(M_1^0)$
k_3 = dimensionless rate constant, = $k_f\theta(M_1^0)$
k_4 = dimensionless rate constant, = $k_h\theta(M_1^0)^{1/2}$
k_5 = dimensionless rate constant, = $k_t\theta$
k_6 = dimensionless rate constant, = $k_s\theta(W)$
M_n = dead polymers containing n monomer units
(M_n) = concentration of M_n
(M_1^0) = feed monomer concentration
MW = monomer molecular weight
P_n = active or live polymer containing n monomer units
(P_n) = concentration of P_n
p = $(P_1)/(M_1^0)$
r_G, r_H defined in Equations (4), (5)
r_{M_n} = rate of formation of M_n
r_{P_n} = rate of formation of P_n
s = parameter in moment generating functions
t = dimensionless time, = real time/θ
u = dimensionless H_2 concentration, = $(H_2)/(M_1^0)$
V = reactor volume
W = solvent or impurity
(W) = solvent or impurity concentration
y = dimensionless monomer concentration, = $(M_1)/(M_1^0)$
y^0 = dimensionless monomer feed concentration
$y^0_{\max}$ = maximum value of y^0
$y^0_{\min}$ = minimum value of y^0

$$z_i = \left.\frac{\partial^i G\,(s,t)}{\partial s^i}\right|_{s=1} \Big/ (M_1^0)$$

Greek Letters

α = fraction of the total mean residence time
γ = fraction of the period in which the minimum H_2 concentration is used
θ = mean residence time of the CSTR
μ_1, μ_2 = first and second moments of the MWD respectively. See Equations (25) and (26)

$$\xi_i = \left.\frac{\partial^i H\,(s,t)}{\partial s^i}\right|_{s=1} \Big/ (M_1^0)$$

σ = recirculation ratio within the CSTR
τ = dimensionless period

Subscripts

R = reaction zone
M = mixing zone

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On the Oxidation of Fuel Nitrogen in a Diffusion Flame

The kinetic mechanisms of fuel nitrogen conversion to NO and N_2 in a diffusion flame were investigated. A simple model of a diffusion flame in which the reaction zone has a finite thickness was developed. The purpose of this model was to allow the testing of complex kinetic mechanisms of pollutant formation under conditions where the fuel and oxidant feed rates are controlled by diffusion. A simple kinetic mechanism in which fuel nitrogen was simulated by nitrogen atoms showed the correct functional dependence of nitric oxide emissions on fuel nitrogen content. The model also predicts a significant effect of combustion intensity and temperature on fuel nitrogen conversion. For the hydrogen air diffusion flame the Zeldovich reaction mechanism could account for the production of N_2 as well as NO.

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SCOPE

When a fuel containing chemically bound nitrogen is burned, the fuel nitrogen is converted partially to NO and partially to N_2. An understanding of the kinetic mechanisms of this process is important since it will hopefully lead to progress in NO_x abatement by combustion modifications.

In real furnace flames the combustion process is exceedingly complex, and pollutant formation is affected not only by the chemistry of combustion but also by the physical processes that control the environment in which the chemistry takes place. It is known that flame characteristics can markedly affect the percent fuel nitrogen converted to NO. One of the pitfalls for a researcher in this field is to apply the results obtained for a premixed system directly to turbulent diffusion flames, only to find that the predicted NO is much higher than that measured in practice. This is because, in the presence of O_2, there is no sufficiently rapid route to form the $N \equiv N$ bond from, say, N atoms.

There is a need therefore to develop a model that allows the investigation of kinetic mechanisms in a turbulent diffusion flame so that the results can be related directly to field operating data. Realistic kinetic mechanisms of pollutant formation, however, usually involve a large number of reactions and reactive species, and the usual steady state or equilibrium assumptions are not valid.

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