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Nonlinear dynamics found in polymerization processes — a review

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Abstract

Each year more than a hundred million tons of polymer are produced worldwide in a variety of polymerization processes. Most of the polymerization reactions involved are highly exothermic so that very interesting and troublesome nonlinear dynamics arise routinely in these processes. In this paper, the key reaction parameters are examined for a variety of important polymers and examples are provided illustrating the steady state multiplicity, sustained oscillations, and traveling waves which can arise in industrial reactors. Among the reactors discussed are stirred tanks, loops, and fluidized beds. Some of the effects of imperfect mixing will also be demonstrated by examples. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymerization; Nonlinear dynamics, Steady state multiplicity; Sustained oscillations; Waves

1. Introduction

The dynamic behavior of polymerization processes is both intellectually fascinating and of great practical importance. Each year more than 100 million tons of synthetic polymers are produced worldwide. The greater part of this production involves processes which can exhibit highly nonlinear dynamic behavior — including phenomena such as multiple steady states, sustained oscillations, and traveling waves. These can be predicted from process models, demonstrated in laboratory reactors, and experienced in a wide range of industrial processes. We shall provide some references to work describing in detail these phenomena; however a comprehensive literature review cannot be provided in the space available here.

Polymerization is carried out by two major classes of mechanisms: (i) *addition polymerization* in which monomer units are added to the growing chain one at a time, and (ii) *condensation polymerization* in which the chains themselves react with each other to increase chain length. From the viewpoint of reactor dynamics, condensation polymerization is not of great interest because heat of polymerization is very small. By contrast, addition polymerization reactions are always highly exothermic and can lead to very exotic dynamics as we shall see.

Another aspect which can play a role in nonlinear dynamics is the number of phases present in the reactor. Many polymers are insoluble in their monomers and common solvents, so that a separate phase may be formed upon polymerization. Furthermore, some processes are designed to operate as suspensions, dispersions, or emulsions. As we know, highly exothermic reactions carried out in particles can lead to multiple steady states and other dynamic phenomena for the particles themselves, and this occurs also in some polymerization processes. Some designers choose to carry out these exothermic polymerizations in submicron particle emulsions with water as the continuous phase. This "water cooling" guarantees that the particles remain isothermal. Nevertheless, these emulsion reactors frequently exhibit multiple steady states and sustained oscillations even under isothermal conditions. Some reviews of these phenomena may be found in Gerrens (1980) and Ray (1981, 1983,1991).

In what follows, we will first discuss the thermodynamic and kinetic parameters which guarantee extreme exothermicity for addition polymerization reactions. Then we will analyze phenomena such as multiple steady states and oscillatory behavior in continuous stirred tank reactors (CSTRs) for polymerization. Finally we will demonstrate these and other phenomena in other types of reactors such as fluidized and loop reactors. An

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important aspect which will be treated also is the effect of imperfect mixing on polymerization process dynamics. Finally, we will discuss *isothermal* multiplicity and oscillatory behavior observed in emulsion polymerization processes and polymer particle multiplicity and overheating issues as well.

2. Multiplicity and oscillations in CSTRs

There are several important kinetic mechanisms which lead to addition polymerization. These are free-radical, ionic and group transfer, and coordination catalyzed polymerization. They differ in important chemical aspects, but are generally similar in terms of the parameters that govern nonlinear dynamic behavior. The general mechanism is summarized in Table 1. All of them involve the *initiation* of an active species, P_0^*, from a precursor with an overall mechanism

$$vI \underset{k_I}{\rightarrow} P_0^*. \tag{1a}$$

This is followed by the general *propagation* step

$$P_n^* + M \underset{k_p}{\rightarrow} P_{n+1}^*, \quad n = 0, 1, 2, \ldots \tag{1b}$$

which means an active, growing polymer chain, P_n^*, reacts with monomer to form a longer growing polymer chain, P_{n+1}^*. Finally, there is a *termination* step to kill the active species; this takes the general form

$$sP_n^* \underset{k_t}{\rightarrow} \text{ dead species.} \tag{1c}$$

As seen in Table 1, both the initiation and termination steps can involve reaction with other species or bimolecular reactions when the stoichiometric coefficients v and s are 2.

The propagation step is the only important one in determining monomer conversion and heat of polymerization because the other steps occur only once per chain while propagation occurs hundreds or thousands of times per chain. The heat of polymerization and adiabatic temperature rise for a particular polymer is nearly independent of the particular kinetic mechanism involved. However, the heat of polymerization does depend somewhat on the state of the monomer (liquid or gas) and the final state of the polymer, (e.g.; degree of crystallinity). As we shall see, these states depend on the particular process being used. Table 2 provides heats of polymerization and adiabatic temperature rise under standard conditions for the most common monomers used by industry. The adiabatic temperature rise, which is the temperature increase resulting from a closed, insulated system reacting to completion, may be determined from

$$\Delta T_{\mathrm{ad}} = \frac{(-\Delta H_p) M_f}{\rho C_p}. \tag{2}$$

The values shown in Table 2 assume pure liquid monomer as the reactant. Note that for most polymers, the adiabatic temperature rise would carry the reactor above the decomposition point of the monomer and polymer — leading to the onset of exothermic side reactions which could increase the adiabatic temperature rise still further. Thus addition polymerization, by any kinetic mechanism, requires careful design to avoid thermal runaway.

Another reactor design parameter, the heat removal duty also is shown in Table 2. Note that there are dramatic variations in heat removal requirements depending on the polymer being produced. For example, polyethylene and polypropylene are produced commercially using similar processes and similar catalysts, yet polyethylene reactors require almost twice the heat removal capabilities at the same production rate. Similarly, vinyl acetate and methylmethacrylate can be polymerized in the same reactors under similar operating conditions, yet vinyl acetate polymerization requires almost twice the heat removal capability as methylmethacrylate polymerization for the same production rate. If one compares ethylene and methylmethacrylate polymerization, one sees that polyethylene production requires seven times the heat removal capacity relative to polymethyl methacrylate production. These considerations are just to satisfy the steady-state energy balance. The possibilities of multiple steady states, oscillations, and other exotic dynamics depend on the particular kinetic mechanism employed. This will be analyzed in detail below.

The dynamic behavior in non-isothermal single-phase reactors is controlled by the energy balance and material balances on monomer, initiator/catalyst, and growing polymer chains. These all intersect in the propagation rate expression

$$R_p = k_p \left[\sum_{n=0}^{\infty} P_n^* \right] [M], \tag{3}$$

where we assume that there are an infinite number of growing polymer chain lengths $n = 0, 1, 2, \ldots, \infty$, but a finite total concentration of growing chains, λ_0, where

$$\lambda_0 = \sum_{n=0}^{\infty} P_n^*.$$

In almost all cases of practical interest, the propagation reaction is irreversible, as we assume here, although in some cases reversible polymerization must be considered.

The relevant material and energy balances for a well-mixed CSTR with wall cooling are as follows:

$$V \frac{\mathrm{d}I}{\mathrm{d}t'} = F(I_f - I) - VR_I, \tag{4}$$

Table 1
Simplified addition homopolymerization kinetics

Initiation	$C + I \rightarrow P_0$
	$P_0 + M \xrightarrow{k_{Pr}} P_1$
Propagation	$P_n + M \xrightarrow{k_P} P_{n+1}$
Chain Transfer: To monomer, Solvent, agent, Or spontaneous	$P_n + \begin{bmatrix} M \\ S \\ A \\ - \end{bmatrix} \xrightarrow{k_{tri}} D_n + P_0$
Association:	
Ionic	$P_n \cdots P_m \underset{k_{r1}}{\overset{k_{f1}}{\rightleftarrows}} P_n + P_m$
Group transfer	$C + Q_n \underset{k_{r2}}{\overset{k_{f2}}{\rightleftarrows}} P_n$
Termination:	
Coupling	$P_n + P_m \xrightarrow{k_{tc}} D_{n+m}$
Disproportionation	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$
Inhibition	$P_n + X \xrightarrow{k_{tx}} D_n(+C$ if applicable)
	$P_o + X \xrightarrow{k_{txr}}$ fragments ($+C$ if applicable)
Spontaneous	$P_n \xrightarrow{k_{tsp}} D_n(+C$ if applicable)

Basic kinetics	Free radical	Ziegler–Natta	Anionic	Cationic	Group transfer
Initiation	●	●	●	●	●
Propagation	●	●	●	●	●
Chain transfer	●	●	○	●	○
Association			●		●
Termination	●	●	○	●	○

●-Usually present.
○-Rarely present.

$$V\frac{d\lambda_0}{dt'} = F(\lambda_{0f} - \lambda_0) - VR_{\lambda_0}, \tag{5}$$

$$V\frac{dM}{dt'} = F(M_f - M) - VR_p, \tag{6}$$

$$V\rho C_p\frac{dT}{dt'} = \rho C_p F(T_f - T) + V(-\Delta H_p)R_p - hA(T - T_c). \tag{7}$$

Here I represents growing chain precursor species such as free-radical initiator, or unactivated catalyst, or inactive ionic species depending on the mechanism under study. Also, we assume constant ρ, C_p, V, F for simplicity and neglect the heats of reaction of the initiation/termination reactions.

The relevant reaction rate expressions are

$$R_I = k_I I, \tag{8}$$

$$R_{\lambda 0} = -(k_I I - k_t \lambda_0^s), \tag{9}$$

where R_I represents the rate of initiation of new growing polymer chains from precursor and $R_{\lambda 0}$ the net rate of disappearance of growing polymer chains. In some cases,

Table 2
Thermal parameters for addition polymerization dynamics

Monomer	Heat poly (Kcal/mol)	Pure mon conc (mol/l)	Adiab. temp rise (°C)	Heat removal duty (Kcal/kg)
Ethylene	25.9	14.2	1609	922
Propylene	20.1	12.3	850	477
1-Butene	19.9	10.6	647	355
Isobutylene	11.5	10.6	395	204
1,3-Butadiene	17.4	11.5	589	322
Isoprene	17.9	10.0	496	263
Styrene	17.4	8.7	398	167
alpha-Methylstyrene	8.4	7.7	173	71
Vinyl chloride	17.2	14.6	803	275
Vinylidene chloride	17.4	12.5	655	180
Tetrafluoroethylene	38.9	15.2	1447	389
Acrylic acid	16.0	14.6	464	222
Acrylonitrile	18.3	15.2	774	344
Maleic anhydride	14.1	15.3	491	144
Vinyl acetate	21.0	10.8	519	244
Methyl acrylate	18.6	11.1	452	216
Methyl methacrylate	13.4	9.4	260	134
Methacrylic acid	15.4	11.8	403	179
Butyl acrylate	18.6	7.0	310	145

Notes: Data is from various sources, conditions are liquid monomer to partially crystalline polymer, Temperature is approx 300 K. In practice there will be some variations in these numbers depending on monomer and polymer state, polymerization temperature and pressure, presence of solvent or diluent, choice of initiator or catalyst, etc.

R_I and $R_{\lambda 0}$ can depend on other species as well. From Eq. (3), the rate of disappearance of monomer by reaction is given by

$$R_p = k_p[\lambda_0][M]. \tag{10}$$

Here we assume that k_p, k_I, k_t have the normal Arrhenius dependence on temperature with activation energies E_p, E_I, E_t, respectively.

3. Dynamics of free-radical polymerization reactors

A very large fraction of synthetic polymers are made industrially through free-radical polymerization. The creation of free radicals is usually from some chemical initiator which decomposes as temperature is increased. As shown in Table 3, the activation energy for this step is quite large, while the activation energies for propagation and for termination are smaller. For free-radical polymerization, the termination step is bimolecular ($s = 2$), and, the chain lifetime is several orders of magnitude shorter than the time scale for monomer disappearance; thus the growing polymer chain concentration may be considered to be in a quasi-steady state with the other quantities and in addition, there is a negligible inflow and outflow of free radicals compared to the reaction terms. In this case, Eqs. (5) and (9) become

$$R_{\lambda 0} = -(k_I I - k_t \lambda_0^2) = 0, \tag{11}$$

$$\lambda_0 = \sqrt{\frac{k_I I}{k_t}} \tag{12}$$

and the dynamic equations have been reduced to Eqs. (4), (6) and (7). If one chooses an initiator which does not decompose to a significant degree over the temperature range of interest and is present in sufficiently high concentration to supply the necessary free radicals, then Eq. (4) becomes $I \cong I_f$, i.e., the reactor concentration is close to the feed concentration. In this case, only the monomer and energy balances are relevant and the model reduces to Eqs. (6) and (7). Thus, R_p in Eq. (10) takes the simplified form

$$R_p = k_p\left(\frac{k_I I_f}{k_t}\right)^{1/2} M = k_{ov} M, \tag{13}$$

where the "overall" rate constant, k_{ov} is

$$k_{ov} = k_p\left(\frac{k_I I_f}{k_t}\right)^{1/2}. \tag{14}$$

Table 3
Thermal and kinetic parameters for free-radical and coordination catalytic polymerization dynamics

Activation Energies Monomer	Initiation, E_i (Kcal/mol)	Propagation, E_p (Kcal/mol)	Termination, E_t (Kcal/mol)	Overall, E_{ov} (Kcal/mol)	γ_{ov}	B-parameter
Ethylene, Free–radical	38.4	7.1	2.4	25.1	41.8	224.4
Ethylene, Ziegler–Natta		10.0		10.0	16.7	89.4
Propylene, Ziegler–Natta		10.0		10.0	16.7	47.2
1-Butene, Ziegler–Natta		10.0		10.0	16.7	36.0
1,3-Butadiene	30.0	5.8	1.9	19.9	33.1	64.9
Isoprene	30.0	9.8	2.0	23.8	39.7	65.6
Styrene	30.0	6.2	1.9	20.3	33.8	44.8
Vinyl chloride	30.0	3.8	4.2	16.7	27.8	74.5
Vinylidene chloride	30.0	9.0	5.0	21.5	35.8	78.3
Tetrafluoroethylene	30.0	4.2	3.3	17.6	29.3	141.1
Acrylonitrile	30.0	3.8	3.7	17.0	28.3	72.9
Vinyl acetate	30.0	6.3	3.2	19.7	32.8	56.8
Methyl acrylate	30.0	7.1	5.3	19.5	32.4	48.9
Methyl methacrylate	30.0	6.3	2.8	19.9	33.2	28.7
Butyl acrylate	30.0	12.5	17.6	18.7	31.2	32.3

Notes: Data are from various sources, conditions are liquid monomer to partially crystalline polymer, temperature is approx 300 K. For γ_{ov} and B, a feed temperature of 300 K is assumed. In practice, there will be some variations in these numbers depending on monomer and polymer state, polymerization temperature and pressure, presence of solvent or diluent, choice of initiator or catalyst, etc.

By defining the following dimensionless parameters:

$$\tau = \frac{V}{F}, t = t'/\tau, \quad Da = k_{ov}(T_f)\tau, \quad \gamma_{ov} = \frac{E_p + \frac{1}{2}(E_I - E_t)}{RT_f}$$

$$B = \frac{\Delta T_{\mathrm{ad}}}{T_f}\gamma_{ov} = \frac{(-\Delta H_\rho)M_f}{\rho c_p T_f}\gamma_{ov}, \quad \beta = \frac{hA}{\rho c_p F},$$

$$x_M = 1 - \frac{M}{M_f}, \quad x_T = \left(\frac{T - T_f}{T_f}\right)\gamma_{ov}, \quad x_c = \left(\frac{T_c - T_f}{T_f}\right)\gamma_{ov}. \tag{15}$$

Eqs. (6) and (7) take the standard dimensionless form

$$\frac{\mathrm{d}x_M}{\mathrm{d}t} = -x_M + Da(1 - x_M)\exp\left\{\frac{x_T}{1 + x_T/\gamma_{ov}}\right\}, \tag{16}$$

$$\frac{\mathrm{d}x_T}{\mathrm{d}t} = -x_T + BDa(1 - x_M)\exp\left\{\frac{x_T}{1 + x_T/\gamma_{ov}}\right\} - \beta(x_T - x_c). \tag{17}$$

The simplified model (16) and (17) is in a form that allows the use of well-known multiplicity and sustained oscillation criteria. For example, the necessary condition for the existence of multiple steady states is (Uppal, Ray & Poore, 1974)

$$B > \frac{4[1 + \beta + (\beta x_c/\gamma_{ov})]^2}{1 + \beta - (4/\gamma_{ov})[1 + \beta + (\beta x_c/\gamma_{ov})]} \tag{18}$$

or to a good approximation whenT_c is close to T_f

$$B > \frac{4(1 + \beta)\gamma_{ov}}{\gamma_{ov} - 4}. \tag{19}$$

In a similar way, the necessary condition for sustained oscillations when γ_{ov} is very large is given by Uppal et al. (1974)

$$B > 3 + \beta + 2\sqrt{2 + \beta}. \tag{20}$$

Note that all of these criteria are satisfied if B is greater than 5–15 depending on x_c, γ_{ov}, etc. This provides a rough guideline to judge whether or not one should expect exotic dynamic behavior from a particular polymerization reactor.

For free-radical polymerization, we list values of B and γ_{ov} for common monomers in Table 3. Note that the parameter γ_{ov} is in the range of 30–40 for essentially all free-radical polymerizations. The values of B for free-radical polymerization are incredibly large as seen in Table 3, ranging from about 30 for methylmethacrylate to more than 200 for ethylene. Obviously exotic dynamics are easily possible for any of these monomers. It is important to realize that the large value of γ_{ov} is due to the large activation energy for the decomposition of free radical initiator. However, the large adiabatic temperature rise contribution to B is independent of the reaction kinetics.

The case where there is significant conversion of initiator is more common in industrial scale reactors where

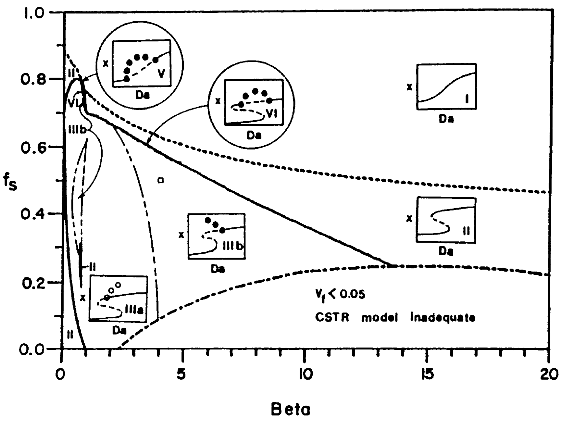

Fig. 1. Parameter space plots for methylmethacrylate homopolymerization (Hamer et al., 1981).

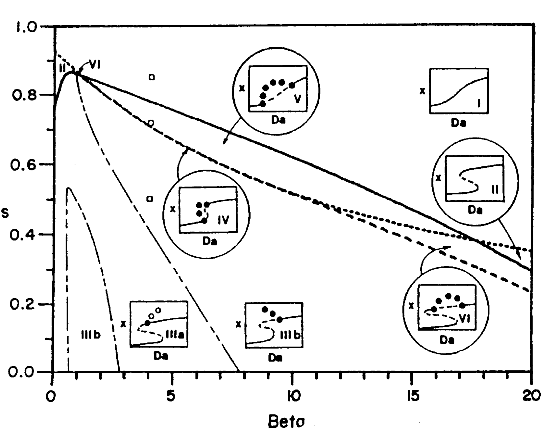

Fig. 2. Parameter space plots for vinyl acetate homopolymerization (Hamer et al., 1981).

it is important not to leave residual initiator in the polymer product. We can analyze this case by using Eq. (12) for λ_0 as before, but by including Eqs. (4) and (8) for I in the dynamic balances. As shown by Teymour and Ray (1989,1991,1992a,b) and Pinto and Ray (1995a,b,1996), this case can have quite an interesting dynamic behavior.

Let us illustrate the types of dynamic phenomena that have been observed in free-radical polymerization reactors. For monomers such as ethylene, methylmethacrylate, vinyl acetate and styrene, multiple steady states and sustained oscillations have been found both from model simulations and from experiment. The experimental work has been guided by detailed parameter space maps such as shown in Figs. 1 and 2 (Hamer, Akramov & Ray, 1981). Here f_s represents the volume fraction of solvent in the feed, which directly influences M_f and thus B. Note the qualitative differences in the parameter space maps between the monomers methylmethacrylate (MMA) and vinyl acetate (VA). MMA has a wide range of conditions where multiple steady states exist, but relatively small regions where we would expect sustained oscillations. By contrast, VA has very large regions where one expects sustained oscillations. These are reflected in the corresponding experiments. To date, no one has reported experiments showing oscillations for MMA in solution polymerization, while many experiments have demonstrated oscillations in vinyl acetate polymerization. Also, various multiplicity structures have been found for these same monomers. Almost any reasonable model will predict S-shaped multiplicities, isolas, and mushrooms. As an example, Fig. 3 shows both model and experimental behavior where there is an isola (Schmidt, Clinch & Ray, 1984). Periodic oscillatory behavior and even periodic isolas and chaos have been found for a wide range of situations (Teymour & Ray, 1991,1992b). Fig. 4 shows that dynamic model predictions and experimental behavior can be quite close.

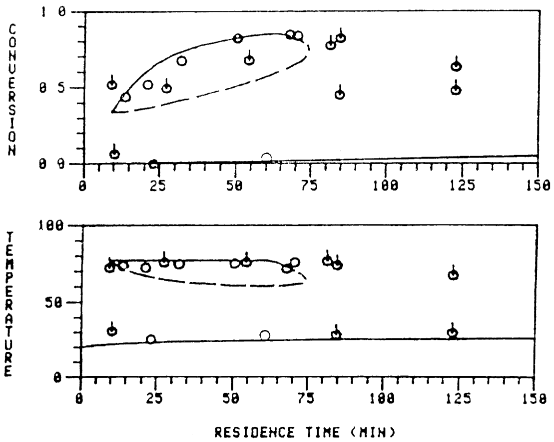

Fig. 3. an isola multiplicity for vinyl acetate homopolymerization model and experiment; $T_f = 20°\text{C}$, $T_c = 25°\text{C}$, $f_s = 0.50$, $I_f = 0.0417$. ○ stable steady state, ⏀ unstable transient (Schmidt et al., 1984).

The influence of small operational changes on the dynamic behavior of solution polymerization can be dramatic. Fig. 5 shows the parameter space plots for VA polymerization with 1% MMA comonomer in the feed. Note the dramatic change from Fig. 2 caused by this small feed composition change. This change also translates into dramatic changes in bifurcation diagrams (cf. Fig. 6) and the on-set or disappearance of oscillations as feed temperature is changed. Fig. 7 shows the onset of oscillations as the feed composition is altered to include 0.25% MMA. Fig. 8 shows oscillations disappearing when the feed composition is changed from 0.375% MMA to pure VA. The presence of ppm levels of free-radical inhibitors such as hydroquinone have a similar effect on reactor dynamics. Fig. 9 shows the bifurcation diagram for varying amounts of inhibitor. Note the small region of five steady states as well as the large region of unique unstable steady states. Fig. 10 shows the onset of

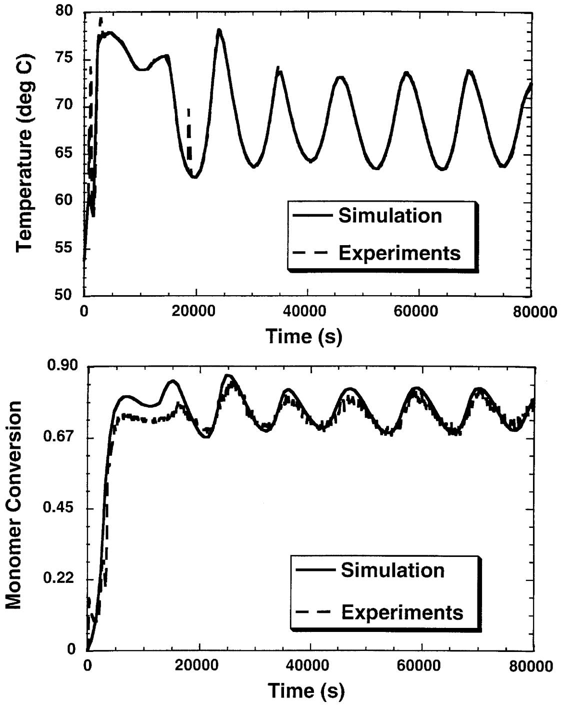

Fig. 4. Oscillations for vinyl acetate homopolymerization — model and experiment. $T_f = 42°C$, $T_c = 45°C$, $f_s = 0.58$, $I_f = 0.038$. Run started at residence time $\tau = 60$ min and switched to $\tau = 90$ min after startup period of 15,000 s (Teymour & Ray, 1989).

oscillations when 80 ppm of hydroquinone is added to the feed.

There are many other examples of multiple steady states or oscillations in free-radical polymerization reactors; however, space does not allow their discussion here.

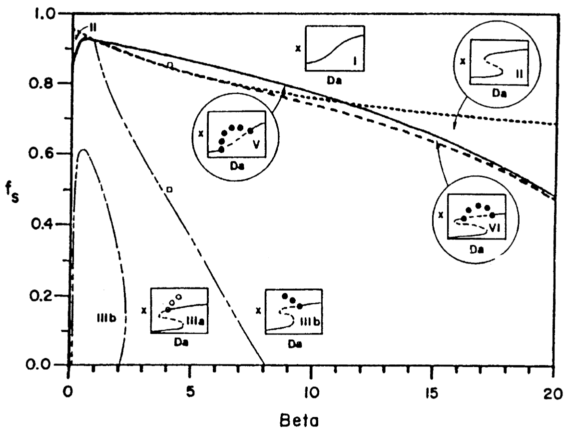

Fig. 5. Parameter space plot for vinyl acetate copolymerization with 1% methylmethacrylate in the feed (Hamer et al., 1981).

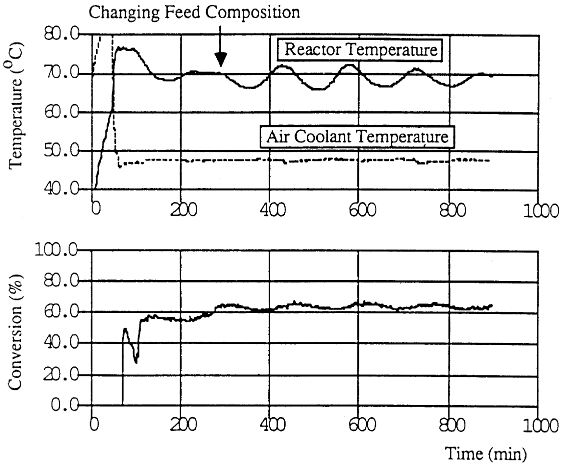

Fig. 7. Onset of oscillations for vinyl acetate polymerization when 0.25% methylmethacrylate is added to the feed (Pinto & Ray, 1995a).

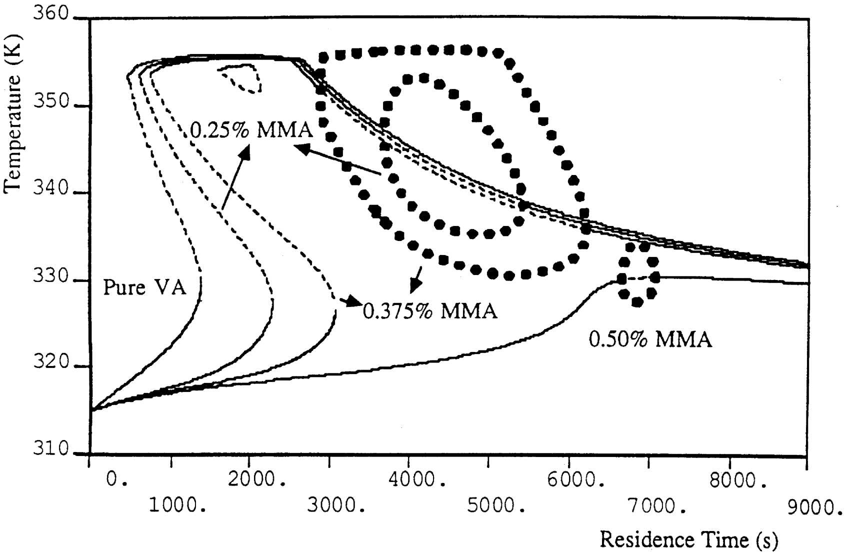

Fig. 6. Bifurcation diagram for vinyl acetate-methylmethacrylate copolymerization (Pinto & Ray, 1995a).

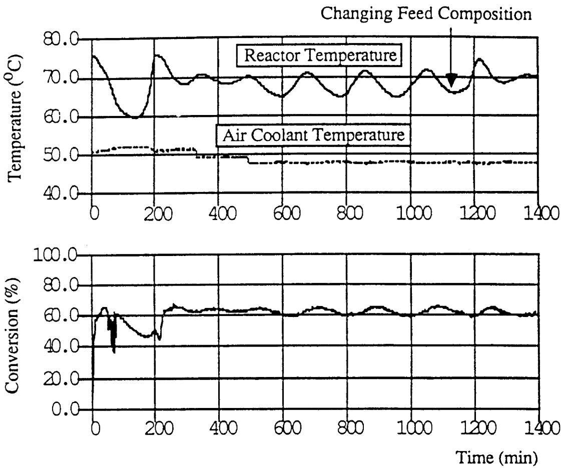

Fig. 8. Cessation of oscillations for vinyl acetate copolymerization with 0.375% methacrylate when feed is switched to pure vinyl acetate (Pinto & Ray, 1995a).

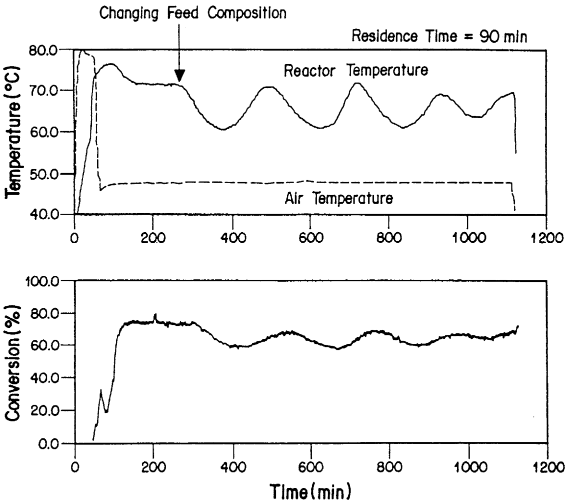

Fig. 10. The onset of oscillations for vinyl acetate polymerization when 80 ppm hydroquinone is added to the feed (Pinto & Ray, 1996).

4. Dynamics of coordination catalyzed polymerization reactors

A second major class of synthetic polymers are polyolefins made by a coordination mechanism using Ziegler–Natta, metallocene, or other catalysts. The reactors can be homogeneous and liquid phase or more commonly can be heterogeneous liquid or gas-phase dispersion processes. Although the polymer particles themselves can have interesting dynamics, this is a separate topic. Here we will use a pseudo-homogeneous model for the heterogeneous reactors. The most common monomers polymerized by this mechanism are ethylene and propylene — representing more than one-third of all thermoplastic polymers produced worldwide (by any kinetic mechanism). We see from Table 2 that the polymerization of these two monomers leads to some of the largest values of heat removal duty and adiabatic temperature rise of all commercial products.

The essentials of the kinetic scheme for these catalyzed polymerizations also can be represented by Eqs. (4)–(10) if we use a pseudohomogeneous model for heterogeneous reactors. In this case, I represents catalyst which is not yet activated, and λ_0 is active catalyst. The initiation step represents catalyst activation which can be spontaneous or can involve monomer, cocatalyst, or other species.

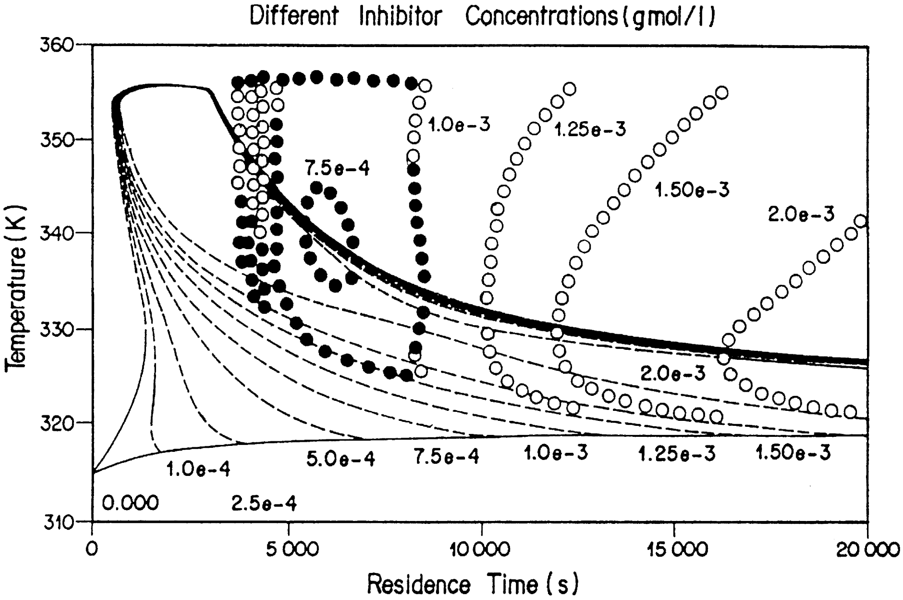

Fig. 9. Bifurcation diagram for vinyl acetate polymerization when there is hydroquinone inhibitor added to the feed (Pinto & Ray, 1996).

The termination step here represents catalyst deactivation which can also depend on other chemical species. Here we assume spontaneous activation and decay for simplicity.

For coordination catalysts, the activation step is usually fast with relatively low activation energy, while the catalyst decay step is usually slow with high activation energy (by catalyst design). For a complete picture of the nonlinear dynamics, all of the four Eqs. (4)–(7) must be considered. However, in the special case where there is very fast catalyst activation and very slow catalyst decay, one can neglect the dynamics of I and λ_0 and only consider the monomer and energy balances (6) and (7) with

$$R_p = k_p I_f M. \tag{21}$$

The dimensionless forms (15)–(17) then apply, if we let $k_{ov} = k_p I_f$ and $E_I = E_t = 0$. In this case, the appropriate values of γ_{ov} and B are given in Table 3 for the monomers ethylene, propylene, and 1-butene. Note that γ_{ov} is moderately large and B is quite large — easily satisfying criteria for multiplicity and dynamic oscillations. As indicated in the table, ethylene is the one polyolefin that is produced both by a free-radical and catalytic route. Because of the high activation energy of the free-radical initiator, the free-radical route has much larger γ_{ov} and B parameters. Next we will illustrate some of the dynamic behavior possible for coordination catalytic processes with a focus on commercial reactor types.

4.1. Liquid-phase reactors

Both solution and liquid slurry reactors are used for olefin polymerization. The solution reactors are used principally for ethylene polymerization and necessarily have high temperatures (150–270°C) and short residence times. These reactors can have interesting dynamics but will not be discussed here. Liquid slurry reactors are used for both polyethylene and polypropylene production. These can be CSTRs or loop reactors. Well-mixed CSTRs can have multiplicity and sustained oscillatory behavior similar to those found for free radical polymerization. Loop reactors at high circulation rates will have the residence time distribution, concentration/temperature uniformity, and nonlinear dynamics of an equivalent well-mixed CSTR. However, if the recirculation rate for the loop is decreased, then spatial non-uniformities can arise and enrich the type of dynamics possible (Zacca & Ray, 1993; Hyanek, Zacca, Teymour & Ray, 1995; Zacca, Zhang & Ray, 1995). Consider the liquid propylene filled slurry loop reactor in Fig. 11. Normally, it will operate stably with a recirculation ratio of 150. However, if an equipment malfunction causes the recirculation rate to drop to 15, the wall heat transfer will be reduced and spatially uniform oscillations will occur as shown in Fig. 12. If the recirculation rate drops further to 4, then there can be significant spatial profiles in the loop, leading to poor utilization of heat transfer area and the onset of traveling waves as shown in Fig. 13.

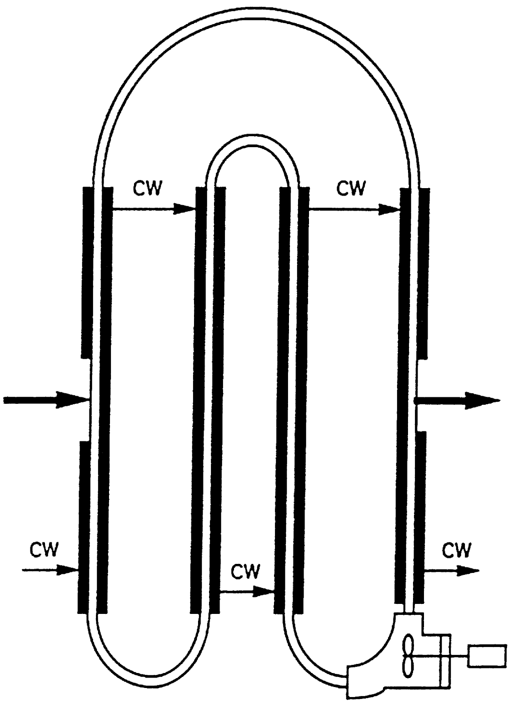

Fig. 11. The loop reactor for olefin polymerization.

4.2. Gas-phase reactors

Gas-phase particle dispersion reactors are very popular for polyethylene and polypropylene production. These include fluidized-bed reactors (Choi & Ray, 1985; Hyanek et al., 1995; Debling et al., 1994), vertical stirred-bed reactors (Choi & Ray, 1988; Debling, Han, Kuijers, VerBurg, Zacca & Ray, 1994), and horizontal stirred-bed reactors (Debling et al., 1994). Each of these reactor types has interesting nonlinear dynamic behavior.

The fluidized-bed process shown in Fig. 14 can include a single reactor or tandem reactors and is used for both polyethylene and polypropylene. The emulsion phase of the fluidized bed contains the polymerizing particles and behaves very much like a well mixed CSTR. Reactor cooling is through a gas recycle stream where gas cooling and perhaps partial condensation takes place. Efforts are made to eliminate particles from the recycle stream. For ethylene polymerization, the presence of hydrogen often reduces catalyst activity, so two different activities are illustrated. Multiplicity in the first reactor may be seen if there is little or no catalyst decay as shown in Fig. 15. However, the model predictions above the polymer melting point are nonsense because fluidization would

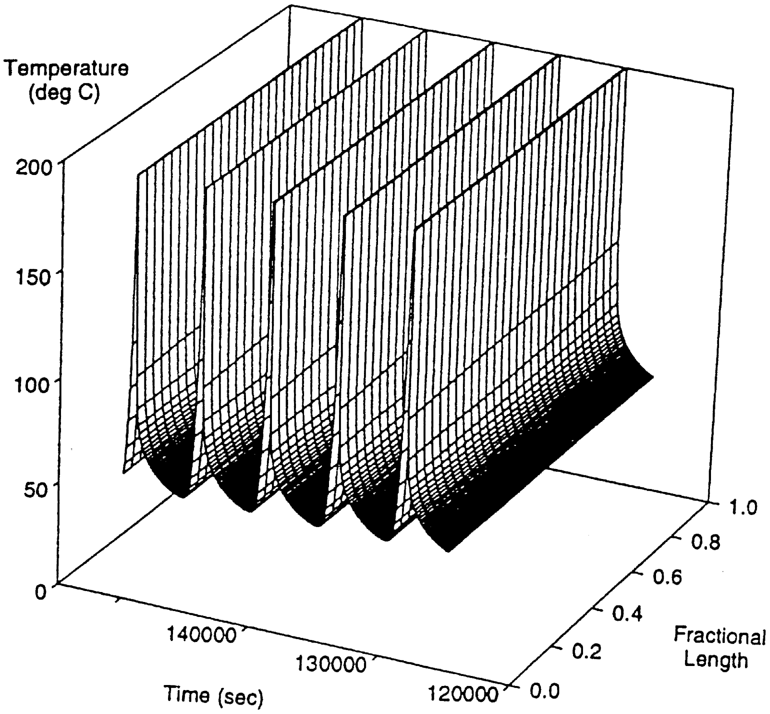

Fig. 12. Spatially uniform sustained oscillations in catalytic propylene polymerization for a recirculation ratio of 15 (Zacca & Ray, 1993).

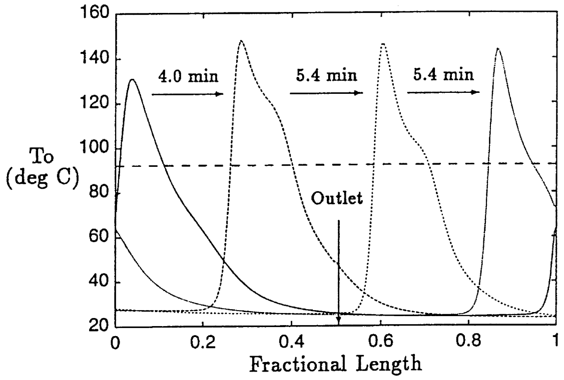

Fig. 13. Nonuniform sustained traveling wave oscillations in catalytic propylene polymerization for a recirculation ratio of 4 (Zacca et al., 1995).

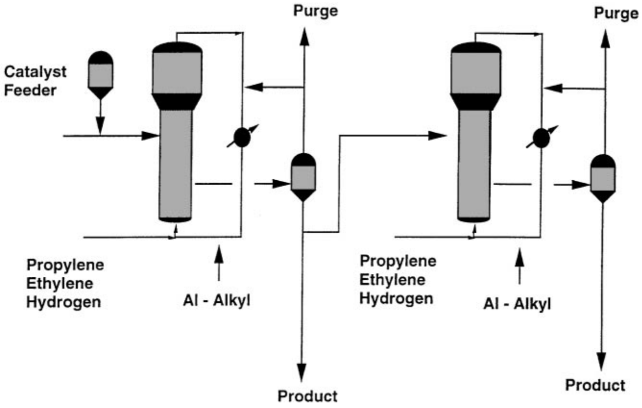

Fig. 14. Fluidized-bed process for polyolefins.

stop and the reactor contents would become molten polymer (which sometimes happens in practice). The relevant behavior below the melting point shows that the reactor would operate on the lower branch which could be unstable due to Hopf bifurcation. With typical parameters for catalyst deactivation, the multiplicity disappears, but a region of unique unstable steady states remains — assuring oscillatory behavior (cf. Fig. 16). As shown in Fig. 17, these oscillations can rise above the polymer melting point, leading to fluidization problems and eventual reactor meltdown. Clearly an understanding of the nonlinear dynamics is essential for safe, effective process operation.

The stirred-bed gas-phase processes also have interesting multiplicity and oscillatory behavior; however, there is no space to discuss these processes in detail here.

5. Effects of mixing on reactor dynamics

There are a number of situations found in practice where imperfect mixing can have a strong effect on reactor dynamics. One of the most common situtation is when the feed material enters a continuous or semi-continuous stirred tank and begins to react before it is

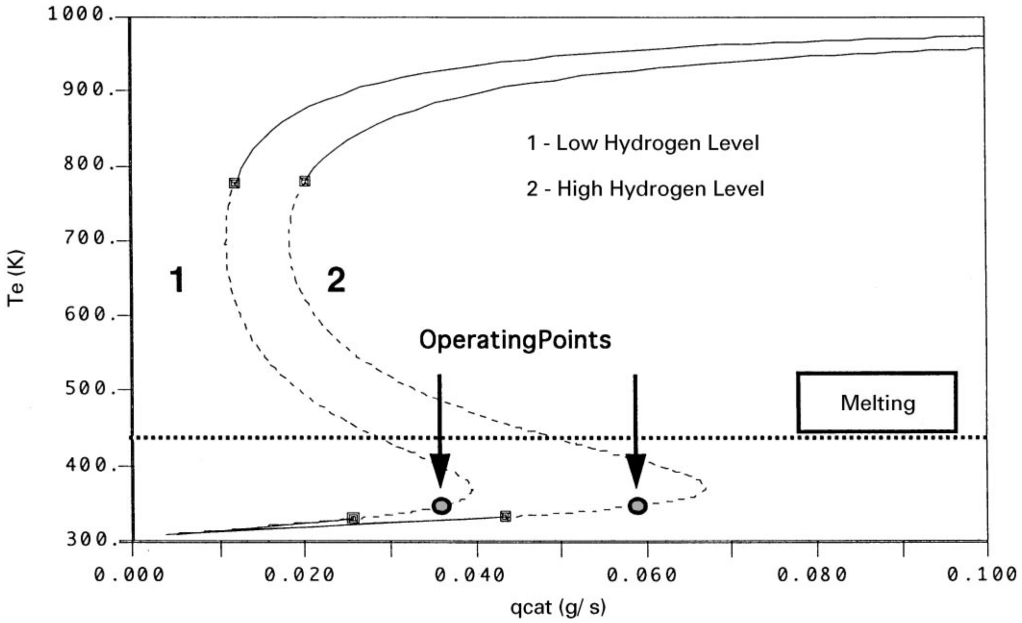

Fig. 15. Bifurcation diagram for two levels of catalyst activity in a polyethylene fluidized-bed reactor — no catalyst deactivation (Hyanek et al., 1995).

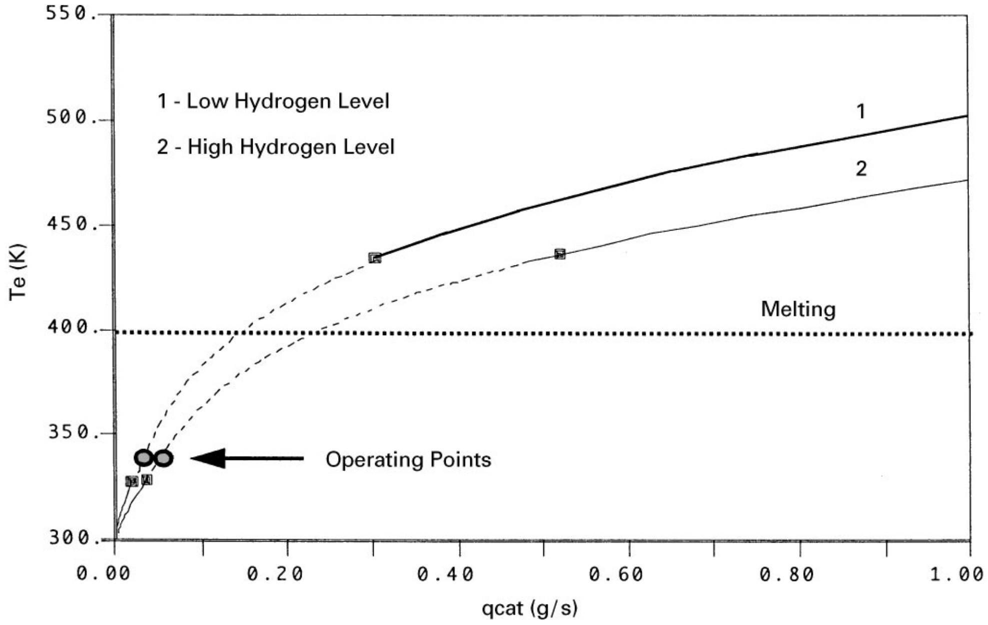

Fig. 16. Bifurcation diagram for two levels of catalyst activity in a polyethylene fluidized-bed reactor — with normal catalyst decay (Hyanek et al., 1995).

completely mixed with the reactor contents. One physical situation is shown in Fig. 18 where a feed plume must be mixed into a well-stirred CSTR. Analysis of this situation may be done by a detailed computational fluid dynamics (CFD) simulations (e.g., Read, Zhang & Ray, 1997) or by appropriate compartment models (e.g., Zhang & Ray, 1997; Villa, Dihora & Ray, 1998) where the various zones of the reactor are represented by an internal flowsheet (cf. Fig. 18, for an example). Let us illustrate the effects of imperfect feed mixing on reactor dynamics and stability through an example.

As we may see in Tables 2 and 3, ethylene polymerization is the most exothermic of the important commercial monomers. In the free-radical autoclave process, (producing a product called low-density polyethylene (LDPE)) the reactor is an adiabatic CSTR with a very short residence time (usually a minute or less). Thus the time scale for reaction at operating conditions is shorter

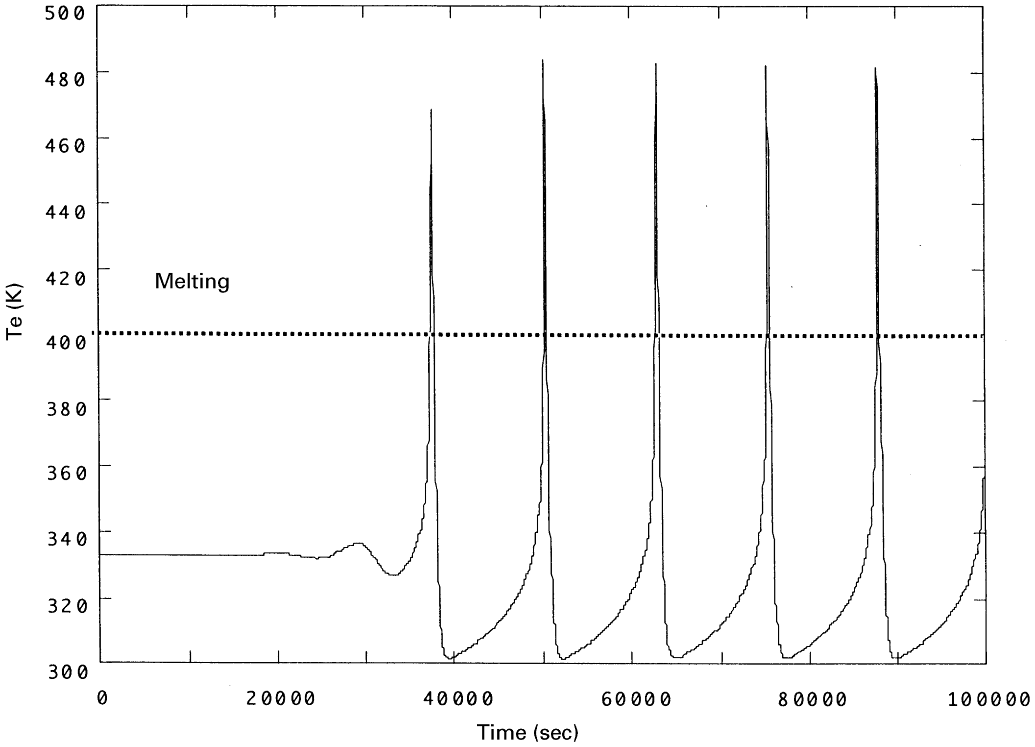

Fig. 17. Fluidized-bed oscillatory dynamics for high hydrogen levels and the operating point shown in Fig. 16 — with normal catalyst decay (Hyanek et al., 1995).

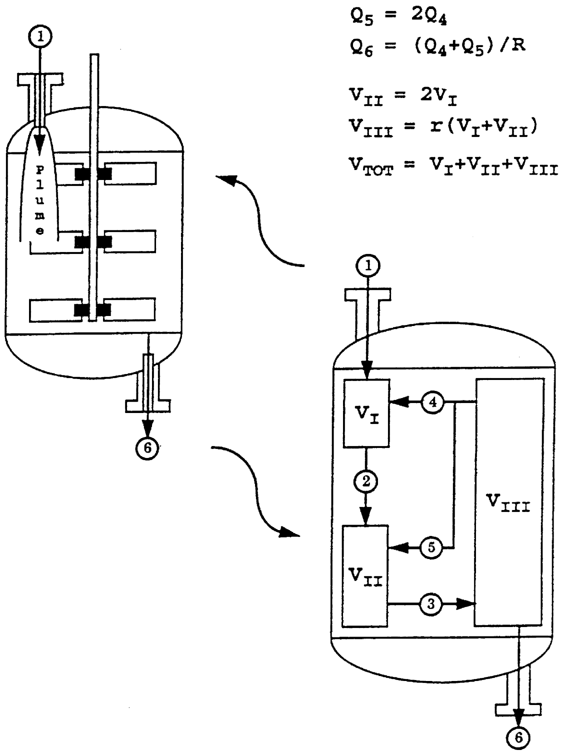

Fig. 18. LDPE autoclave reactor and compartment mixing model (Villa et al., 1998).

than the time required to mix the feed plume with the reactor contents, and an imperfect mixing model is required to predict the behavior of the reactor.

Unfortunately, for ethylene polymerization, there are also highly exothermic, spontaneous ethylene decomposition reactions (Zhang, Nolan & Ray, 1996) which become dominant above ~ 310°C. Thus finding a stable reactor operating condition can be difficult. To illustrate, Fig. 19 shows the bifurcation diagram when there is perfect mixing. Note the tiny stable branch around 250°C which is all that is available for economically reasonable operation. With such a small operating window, the smallest variation in residence time can drive the reactor either to extinction at the lower unreactive steady state, or to explosive runaway. Unfortunately, both of these events occur all too frequently in industrial LDPE reactors.

When one relaxes the perfect mixing assumption and uses the simple compartment model shown in Fig. 18 to represent mixing of the feed plume, the bifurcation diagram changes dramatically. Fig. 20 illustrates the effect of the recirculation parameter R (defined in Fig. 18) on the bifurcation diagram. Physically, R is the number of times, on average, a volume of fluid mixes with the feed plume before exiting the reactor. Thus very high values of R represent perfect mixing, while lower values allow the

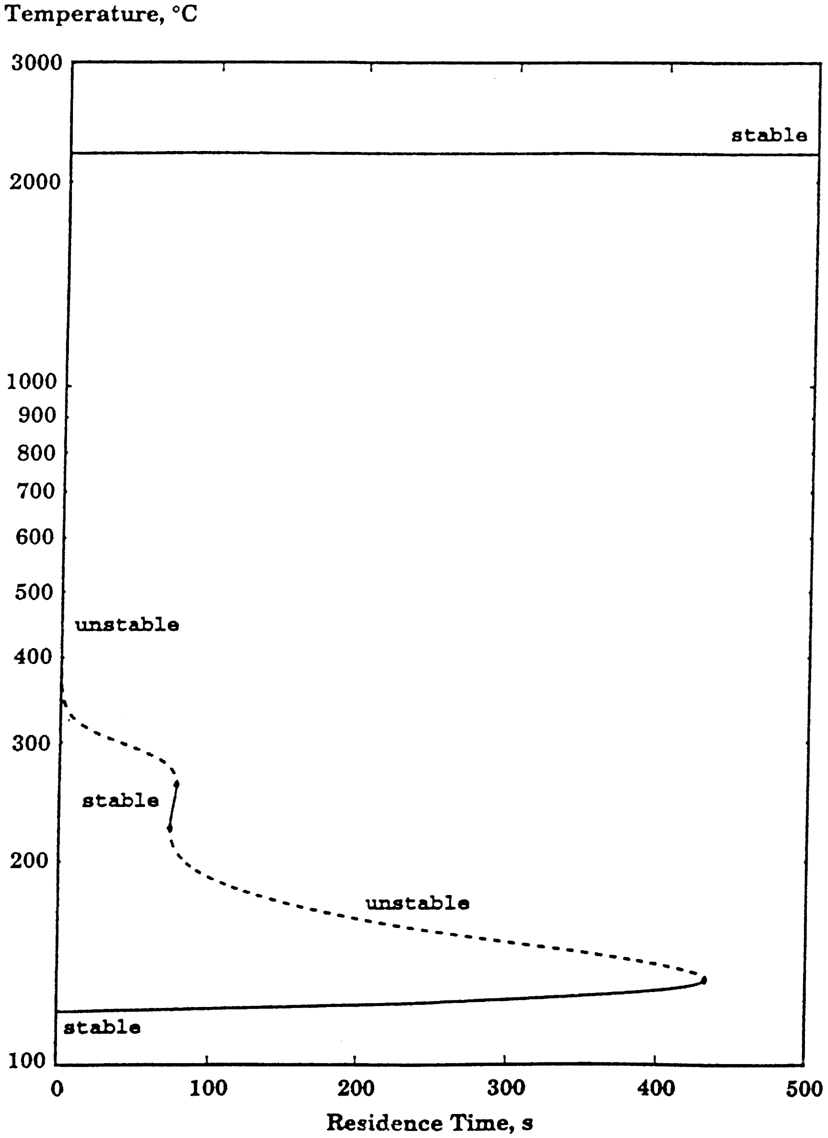

Fig. 19. Bifurcation diagram for the case of perfect mixing (Villa et al., 1998).

modeling of various degrees of imperfect mixing. It has been found that R in the range 5–20 matches data from some industrial reactors. The fact that imperfect mixing greatly enlarges the region of stable operation is of great practical value. As discussed, more detail in (Villa et al., 1998), agitator design, feed location and pipe diameter, as well as the selection of free-radical initiators can have a large effect on reactor stability.

6. Other Nonlinear phenomena

There are other important nonlinear phenomena arising in polymerization processes; however, space does not allow a detailed discussion here. We will simply provide a general description and references for the reader.

6.1. *Isothermal multiplicity and oscillatory behavior*

In some processes, such as continuous emulsion polymerization, there can be multiple steady states and sustained oscillations even when the reactor remains at a constant temperature. The multiplicity arises because of an autocatalytic free-radical reaction step, termed the “gel effect”, which can be strong enough to produce multiple steady states for some monomers (Gerrens, 1980; Rawlings, Prindle & Ray, 1986). The sustained oscillations, frequently observed even in industrial scale emulsion polymerization reactors are the result of competitive particle nucleation and particle growth phenomena similar to the situation in continuous crystallizers. Stability criteria and controllability conditions have been derived and tested for various monomers

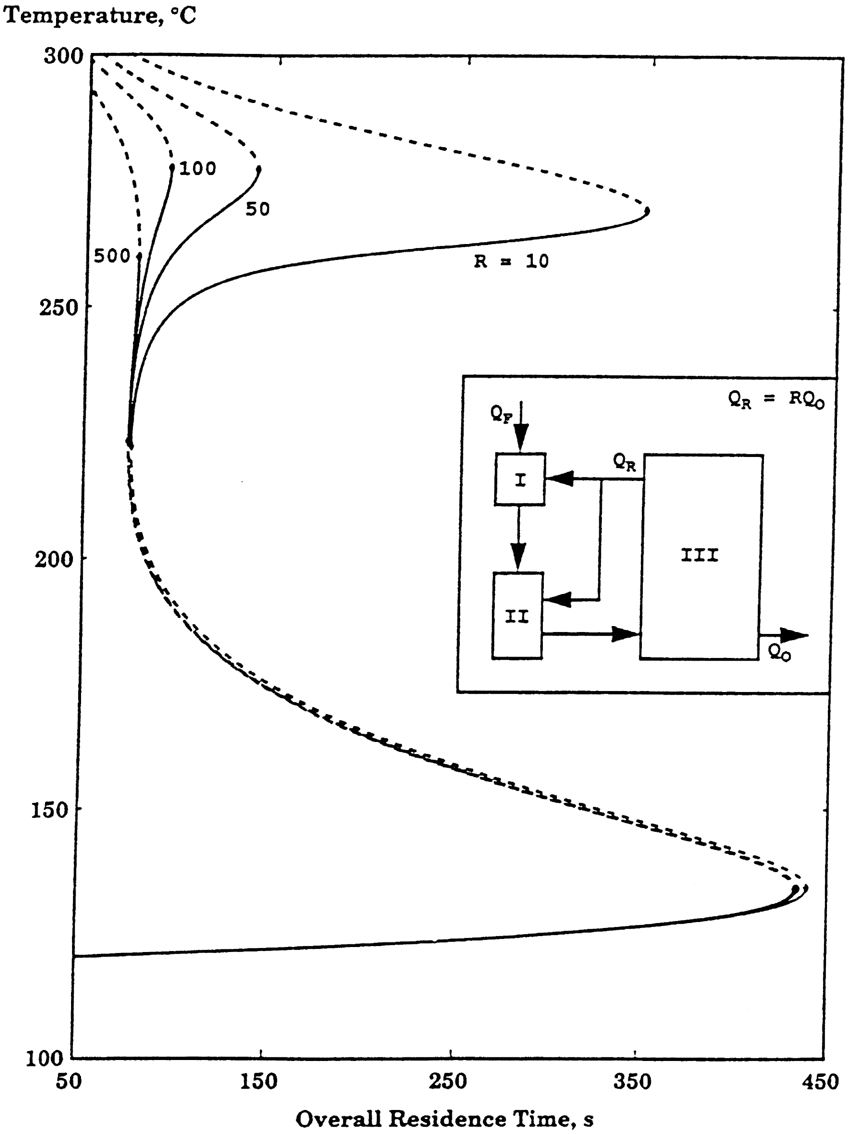

Fig. 20. Bifurcation diagram for the case of imperfect mixing (Villa et al., 1998).

and types of operating conditions (Rawlings & Ray, 1987a,b; Semino & Ray, 1995a,b).

6.2. Particle phenomena

In particle dispersion reactors, the polymer particles themselves can have interesting and important nonlinear dynamics even when the continuous phase composition and temperature remains constant. These phenomena are especially critical in liquid and gas phase olefin polymerization because the polymer particles can overheat and melt even when there is no global reactor overheating. A simple illustration of these effects is discussed in Hutchinson and Ray (1987).

7. Concluding remarks

In this survey paper, a great variety of polymerization processes are discussed for which multiple steady states, sustained oscillations, and other nonlinear phenomena arise routinely in industrial practice. Table 4 illustrates, for five commodity polymers, the variety of reactor types and the huge economic importance of these highly exothermic polymerizations. The particular nonlinear behavior found depends on the polymer produced, the type of polymerization kinetics, the reactor type, the phase behavior, the heat removal system, and even the agitator design. Thus understanding these phenomena is a challenging and important task for the practicing polymerization reaction engineer.

Table 4
Worldwide production in some highly exothermic processes

Monomer	Process	Production (million tons/yr)
Ethylene	Free-radical LDPE in tank and tube reactors (solution reactors)	17
Ethylene	Coordination catalytic HDPE and LLDPE in tank, loop, and fluidized-bed reactors (solution, liquid or gas dispersions)	29
Propylene	Coordination catalytic PP in tank, loop, fluidized, and stirred-bed reactors (liquid or gas dispersions)	20
Styrene	Polystyrene and copolymers in tank reactors (solution, suspension, emulsion)	12
Vinyl chloride	PVC in tank reactors (suspension, emulsion)	20

Note:
LDPE Low-density polyethylene,
HDPE High-density polyethylene,
LLDPE Linear low-density polyethylene,
PP Polypropylene,
PVC Polyvinylchloride.

8. For further reading

The following references are also of interest to the reader: Gerrens (1982) and Ray (1986).

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