

# Polymerization Reactor Control

W. Harmon Ray

**ABSTRACT:** The principal difficulties in achieving good control of polymerization reactors are related to inadequate on-line measurement, a lack of understanding of the dynamics of the process, the highly sensitive and nonlinear behavior of these reactors, and the lack of well-developed techniques for the control of nonlinear processes. Some illustrations of these problems and a discussion of potential techniques for overcoming some of these difficulties are provided.

## Introduction

The topic of polymerization reactor control is so vast and the issues so complex that a comprehensive discussion and literature survey is impossible in the few pages available here. The reader should see Refs. [1], [2] for a survey of the literature in this area. The goal of the present paper is to provide perspective on the important practical problems that arise in the control of polymerization reactors and some useful applications of process control theory to the solution of these problems.

## Control Problems

The "control" problems that arise in operating polymerization reactors are ultimately related to maintaining safe reaction conditions and achieving the specified *production rate* and *quality* of the desired product. However, these problems often take on more distinct forms, and these will be discussed in the following sections.

### *Definition and Monitoring of Product Quality*

Product quality is a much more complex issue in polymerization than in more conventional short-chain reactions. Because the molecular architecture of the polymer is so sensitive to reactor operating conditions, upsets in feed conditions, mixing, reactor temperature, etc., can alter critical molecular properties such as molecular weight distribution, polymer composition distribution, chain-sequence distribution, degree of chain branching, and stereoregularity. In addition, the morphological form of the polymer is

often a key quality variable. For example, the particle-size distribution in emulsion, suspension, and precipitation polymerization can be a crucial product specification. One of the greatest difficulties in achieving quality control of the polymer product is that the actual customer specifications may be in terms of nonmolecular parameters such as tensile strength, crack resistance, temperature stability, color or clarity, absorption capacity for plasticizer, etc. The quantitative relationship between these product-quality parameters and reactor operating conditions may be the least understood area of polymerization reaction engineering. Table 1 summarizes both types of quality control measures.

For most of these product-quality measures (molecular or otherwise), no on-line sensors exist. Thus, it is extremely difficult to control polymer product quality when all that is available are infrequent and delayed measurements, which come from samples sent to the lab. Consequently, there is a desperate need for more on-line sensors for product-quality monitoring. Some recent efforts in this area include on-line conversion, surface tension, and molecular weight measurement (e.g., [3]–[6]).

### *Special Temperature and Reactant Feed Programs for Batch Processes*

Many polymerization processes still involve batch reactors. Thus, the dynamics are nonautonomous, and the product properties result from an integral average of reaction conditions, which change over the batch time. This requires special time-varying temperature and reactant feed programs in order to produce the polymer properties desired. Successful reactor control requires calculation of this special set-point program and often the use of feed measurements and variable gain controllers to implement the desired program. A typical situation involves programming the addition of the more reactive monomers in order to keep polymer composition uniform in copolymerization (e.g., [7]–[10]). Other types of procedures will be discussed later.

### *Nonlinear Steady-State Behavior and Parametric Sensitivity*

Before considering process dynamics, one should note that the steady-state structure of most continuous polymerization reactors is extremely sensitive to small changes in pro-

cess parameters or operating conditions. To illustrate, consider the polymerization of vinyl acetate in a continuous stirred tank reactor (CSTR) under the conditions shown in Fig. 1 [11]. Note that for a jacket cooling temperature of 25°C, there is very complicated steady-state behavior as the mean residence time (feed flowrate) is varied. There are two regions of multiple steady states—one of them an isolated branch (*isola*), which can only be reached with special start-up procedures. Close to the ignition and extinction points, the steady state is quite sensitive to small variations in reaction residence time. To illustrate the extreme sensitivity to other parameters, consider Fig. 2, which shows the effect of  $\pm 2^\circ\text{C}$  variations in cooling jacket temperature. Note that the steady-state structure *changes completely* with these small process parameter variations. Similar behavior is observed with small disturbances in initiator feed concentration or ppm impurities in the feed material. If the control system contemplated manipulating the jacket temperature in response to measured reactor temperature, Fig. 2 shows how nonlinear the process gain is for much of the operating range. Thus, it would be a cruel assignment to design a control system for this reactor. In practice, one would normally choose an alternate design to mitigate this extreme parametric sensitivity. (For this reactor, this can be accomplished by feeding a higher percentage of solvent to reduce reaction viscosity.) This type of nonlinear steady-state behavior also arises in many other types of polymerization reactors (e.g., [3], [12]).

### *Nonlinear Process Dynamics and Reactor Runaway*

In addition to the highly nonlinear steady-state structures found for these reactors, there are often exotic process dynamics (such as autonomous oscillations) and potential reactor-runaway problems. To illustrate, consider the same vinyl acetate polymerization reactor discussed above. The bifurcation structure for homopolymerization is shown in Fig. 3 where  $f_s$  is the fraction of solvent in the feed and  $\beta$  is the heat-transfer capability per unit volume of reactor [13]. The steady-state conversion,  $x$ , versus Damköhler number,  $Da$ , is sketched for each region. For parameters in region V, part of the unique steady-state range is unstable and gives rise to autonomous oscillations, as shown in Fig. 4. To illustrate how the occur-

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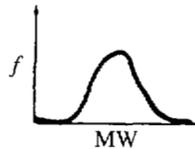
**Table 1**  
Some Measures of Polymer Product Quality

**End-Use Properties**

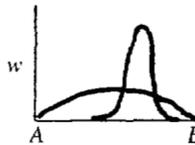
- Flow properties (film blowing, molding, etc.)
- Strength
- Stress crack resistance
- Color, clarity
- Melting point
- Corrosion resistance
- Abrasion resistance
- Density
- Impact resistance
- Temperature stability
- Swellability
- Plasticizer uptake
- Spray-drying characteristics
- Coating and adhesion properties

**Molecular Architecture**

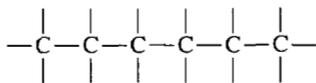
- Average molecular weight and molecular-weight distribution (or melt index, viscosity, etc.)



- Polymer composition and composition distribution



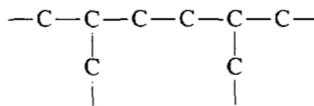
- Chain-sequence distribution
- Degree of chain branching
- (a) Linear:



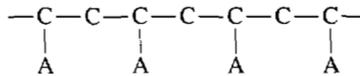
- Stereoregularity (tacticity)



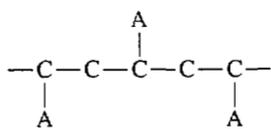
- (b) Branched:



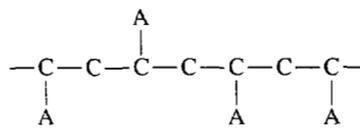
- (a) Isotactic:



- (b) Syndiotactic:



- Average particle-size distribution



- (c) Atactic:

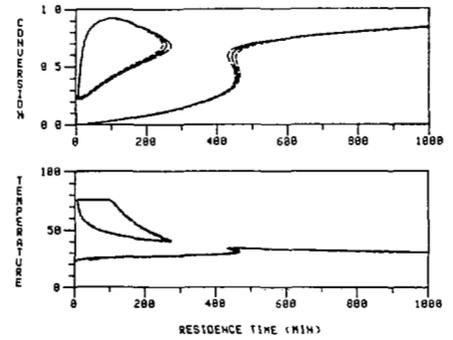
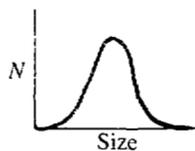


Fig. 1. Steady-state conversion and temperature for vinyl acetate polymerization in a CSTR as a function of reactor residence time [11].

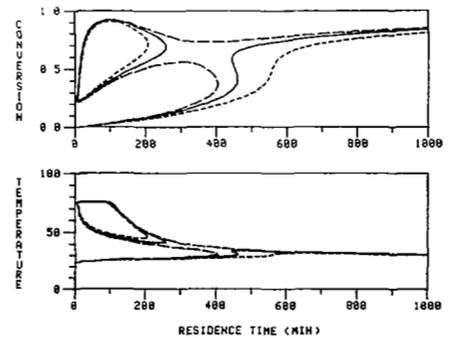


Fig. 2. The effect of small coolant temperature variations on the steady-state behavior for VA polymerization in a CSTR [11]. (—)  $T_c = 25^\circ\text{C}$ ; (---)  $T_c = 23^\circ\text{C}$ ; (- - -)  $T_c = 27^\circ\text{C}$ .

small change in feed composition has drastically altered the reactor dynamics. Such exotic dynamics are common in polymerization processes (e.g., [1], [3], [12], [14]).

Sometimes, this highly nonlinear steady-state and process-dynamics behavior leads to safety and reactor-runaway problems. Although a number of examples exist for solution polymerization, let us illustrate this with the behavior of a fluidized bed for ethylene polymerization shown in Fig. 6 [12]. With manual temperature control, the steady-state behavior as a function of catalyst injection rate is shown in Fig. 7. Note that there is steady-state multiplicity as well as a Hopf bifurcation point on the lower branch beyond which the reactor is unstable. The practical operating range is below the horizontal dot/dashed line at  $\sim 400^\circ\text{K}$ , which represents the softening point of the polymer. Operation above this temperature results in serious melting of polymer and reactor failure. Thus, close control of temperature is important. As shown in Fig. 8, even under feedback control, the process is so sensitive that an in-

rence of such oscillations is sensitive to small process variations, consider the operating parameters  $f_s = 0.855$ ,  $\beta = 4$ . For vinyl acetate homopolymerization (Fig. 3), the bifurcation diagram shows a unique, stable steady state, always. However, if the polymer product required a small amount of com-

onomer, methylmethacrylate, so that the feed-monomer composition is changed to 99 percent VA, 1 percent MMA, the bifurcation structure changes dramatically, thus, the operating point  $f_s = 0.855$ ,  $\beta = 4$ , can now become unstable and can lead to oscillations, as shown in Fig. 5. Therefore, a

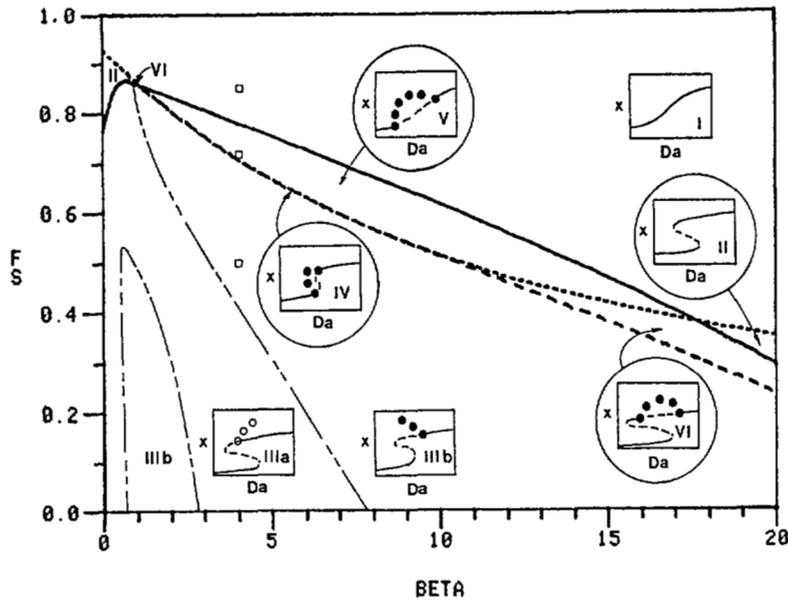


Fig. 3. Bifurcation structure for the homopolymerization of VA in a CSTR [13].

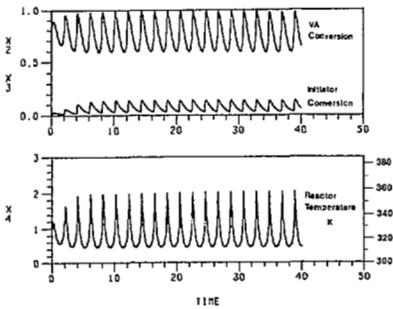


Fig. 4. Open-loop dynamics for VA homopolymerization in a CSTR [13];  $\beta = 4$ ,  $f_s = 0.72$ ,  $Da = 0.15$ .

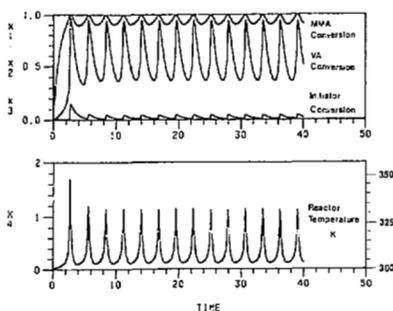


Fig. 5. Open-loop dynamics for VA-MMA copolymerization (99 percent VA, 1 percent MMA) in a CSTR [13].  $\beta = 4$ ,  $f_s = 0.855$ ,  $Da = 0.8$ .

crease in catalyst activity could cause the reactor to reach the limits of the process cooling system and after  $\sim 20$  hours suddenly to runaway with concomitant meltdown of the polymer in the reactor.

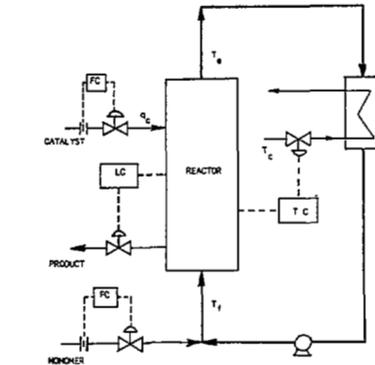


Fig. 6. Control system for the polymerization of ethylene in a gas-phase fluidized bed reactor [12].

### Some Solutions

In the last section, we presented a few of the more striking special problems encountered in the control of polymerization reactors. One can see that these present unusual challenges to the engineer who must design control systems for these reactors. In this section, we will discuss some approaches to control system design that show potential as good solutions.

#### Prediction of Polymer Properties Through Nonlinear State Estimation

One approach that shows promise is to modify nonlinear state estimators (such as the extended Kalman filter) so as to integrate both available on-line measurements and infrequent measurements from lab samples. Early work in the application of state esti-

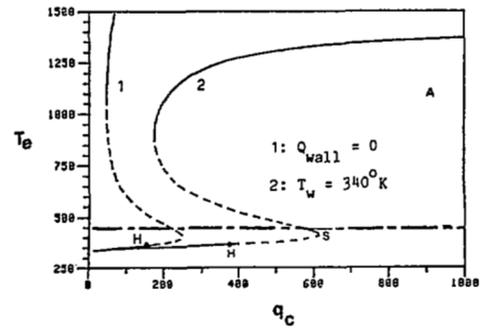


Fig. 7. Steady-state fluidized bed temperature under open-loop temperature control ( $T_f$  fixed) as a function of catalyst injection rate [12]. Curve 1: adiabatic operation; Curve 2: wall cooling,  $H$  — Hopf bifurcation point.

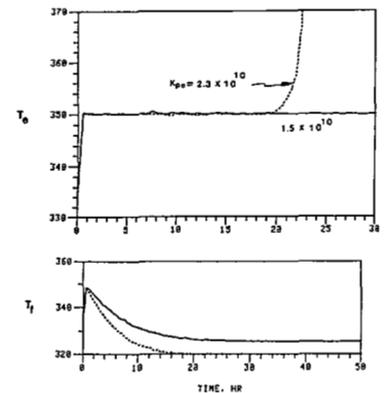


Fig. 8. Fluidized bed start-up behavior under closed-loop temperature control with cooling system capacity constraint  $T_f \geq 320^\circ\text{K}$ . Effect of a 50 percent disturbance in catalyst activity or feed rate [12].

mation to polymerization reactors [15]–[17] demonstrated the feasibility with a few on-line instruments. More recent works (e.g., [18]–[20]) demonstrate the possibilities with a wider range of process measurements and through incorporation of delayed lab measurements into the estimator. The idea is to use the estimated polymer properties in the feedback control scheme so as to reduce variability in polymer product quality.

To illustrate some of the issues (see [20] for a more detailed discussion), Table 2 lists some of the properties that are observable or detectable from the indicated measurements. Note that we have not included all possible combinations of measurements in this simplified table. As indicated, monomer and initiator conversion are readily observable from temperature measurements, but molecular weight or chain-branching properties require

**Table 2**  
**Polymer Property Observability or Detectability Through**  
**State Estimation with Various Sensors [20]**

Measurements	MC	IC	MWD		Branching	
			$M_N$	$M_w$	$B_N$	$B_w$
Temperature	O	O	D	D	D	D
Temperature and refractive index	O	O	D	D	D	D
Temperature and density	O	O	D	D	D	D
<sup>†</sup> Bulk viscosity	O	O	O/D	O	D	O/D
<sup>†</sup> Intrinsic viscosity	O	O	O/D	O	D	O
<sup>†</sup> Low-angle light scattering	O	O	D	O	D	O
<sup>†</sup> Conventional GPC	O	O	O	O	D	O
<sup>†</sup> Multidetector GPC	O	O	O	O	O	O

MC Monomer conversion.

IC Initiator conversion.

<sup>†</sup> Assumes temperature plus refractive index (or density), plus the measurement indicated.

O Observable.

D Detectable.

O/D Observable or detectable depending on model chosen for measurement.

additional measurements. Observability is the desired property because detectability (observation of unstable modes only [21]) leads to good estimates only in steady state. From a practical point of view, observability is a much more desirable property than detectability, because of the sluggish dynamic convergence of estimates that are only detectable. This may be illustrated by some examples taken from methylmethacrylate polymerization in a CSTR [20]. Figure 9 shows the performance in estimating conversion from temperature measurements alone. Figure 10 compares the estimates of  $M_w$  (average molecular weight) with a bulk viscosity sensor ( $M_w$  observable) and without this sensor ( $M_w$  only detectable). Note how much better the estimates are if the system is observable. Obviously, if one has good initial estimates of properties that are only detectable, then there will be somewhat better estimates than shown here.

When one may incorporate both on-line and off-line delayed measurements into the estimator, the results can be quite good. To illustrate, consider the case of vinyl acetate polymerization in a CSTR. Here, we wish to incorporate on-line measurements (temperature, refractive index) together with intrinsic viscosity and GPC measurements coming from the lab with a 90-min delay in results. Figure 11 shows how the estimates for  $M_N$ ,  $M_w$ , and  $B_w$  converge with these delayed measurements. Note that, initially, we must use the predictor estimates (solid

line) until the first lab measurements arrive; then the previous 90 min are corrected (dotted line), and a new predictor estimate is used until a new lab measurement arrives 90 min later. This type of estimator provides an optimal state estimate at each instant, given the data available at that time. Hopefully, this will prove to be a valuable tool in bridging the gap resulting from unavailability of on-line sensors.

#### Detection of Reactor-Runaway Conditions Through State Estimation

There is currently great interest in the chemical industry in preventing runaway reactions, which may lead to reactor failure or even catastrophic damage (such as in the Bhopal disaster). State estimation offers promise in some situations in providing early detection of abnormally dangerous conditions so that preventive action is possible. Early work in this area has been done by Schuler [22], who looked at processes with highly exothermic secondary reactions. Profitable applications in polymerization would

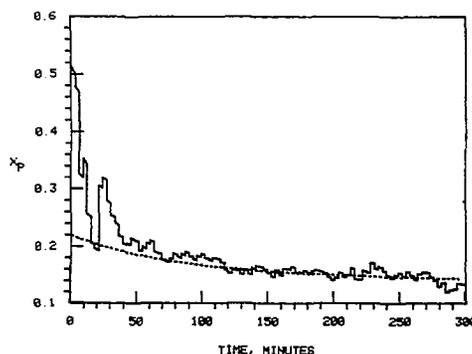


Fig. 9. State estimation of conversion based only on temperature measurements for MMA polymerization in a CSTR [20]. ---- actual, ——— estimated.

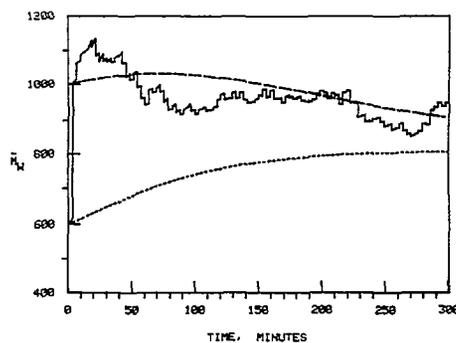


Fig. 10. Comparison of state estimates of  $M_w$  with and without bulk viscosity as a sensor. ——— actual, ——— estimated, ---- detectable only.

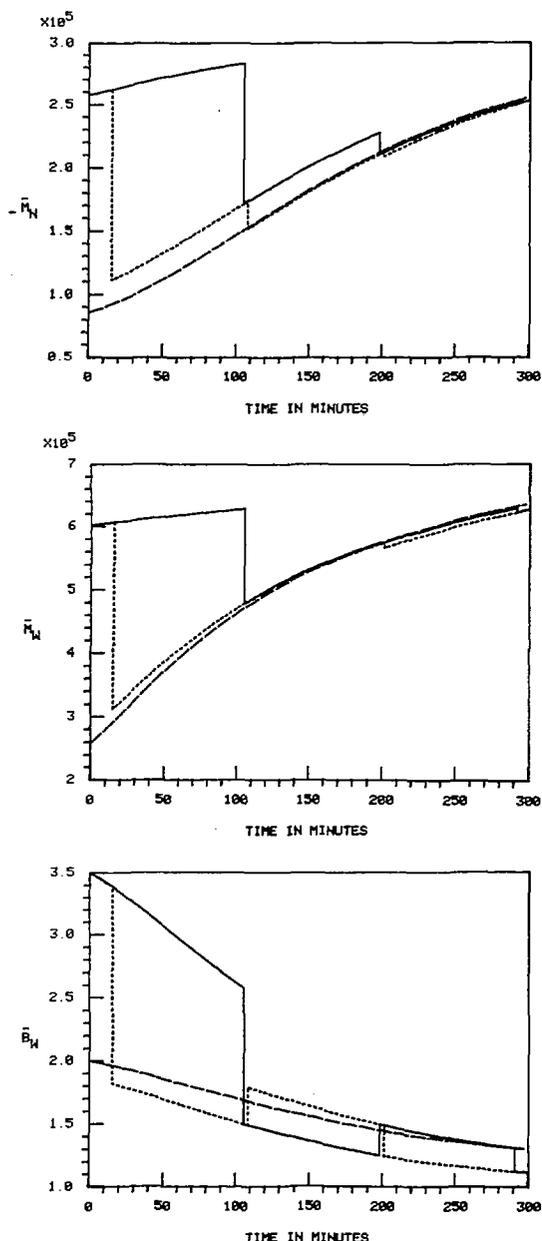


Fig. 11. State estimation of molecular-weight distribution ( $M_N$ ,  $M_W$ ) and degree of branching ( $B_W$ ) incorporating both on-line sensors (temperature and refractive index) plus delayed GPC and intrinsic viscosity measurements from the lab [20] (— actual, — prediction, - - - correction).

include situations such as those shown in Fig. 8, where such mistakes in catalyst addition could be readily detected through state estimation and preventive actions taken well before runaway occurs.

#### Optimal Trajectories for Batch Systems

As discussed above, tailoring of polymer properties often requires the optimal choice

of operating conditions. This requires special optimization techniques for the calculation of these strategies and special variable gain controllers to implement them. Some examples include the optimal choice of conditions to produce the desired molecular-weight distribution at high polymer conversion (e.g., [23]) and the optimal program for monomer and initiator addition to achieve the desired

copolymerization composition distribution [7]–[10]. There is a need to develop routine, systematic procedures for calculating these trajectories for any desired polymer specifications in order to make these techniques readily accessible to the practicing engineer.

#### Techniques for Nonlinear Multivariable Controller Design

From the examples presented in the first section of this paper, it is clear that polymerization reactors are highly nonlinear with exotic dynamics and often great parametric sensitivity. Thus, the feedback controllers required for these processes must be able to perform well at a range of operating conditions even in the face of strong nonlinearities. That is an as yet unmet challenge to the control engineer. Control strategies that incorporate gain scheduling or other adaptive controller features have been proposed (e.g., [24]–[26]), but practical experience with these has been limited. There is still much to be done in this area.

#### Conclusions

Some of the issues arising in polymerization reactor control have been addressed in this paper. As indicated in this discussion, there are many difficult control problems remaining that require a variety of talents to overcome. More and better on-line sensors are needed; more experience with the application of state estimation is required; and finally, better nonlinear and adaptive controllers must be found to deal with the diabolical dynamics arising in most polymerization processes.

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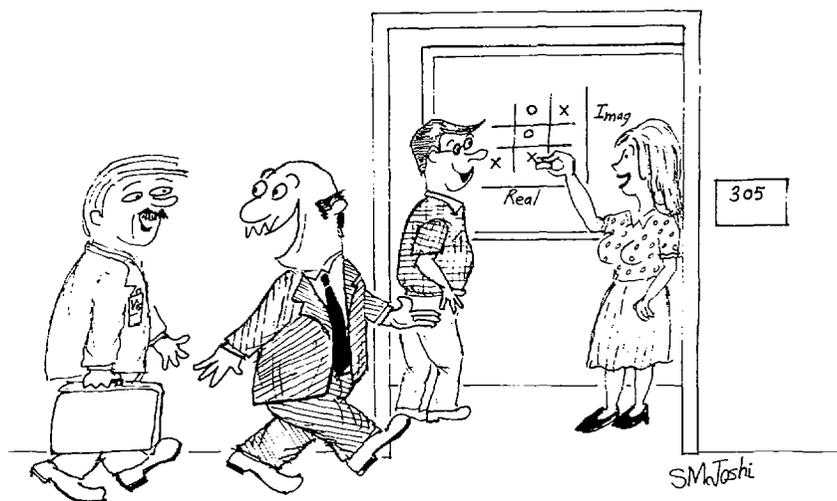
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**W. Harmon Ray** is Professor and Past Chairman of the Department of Chemical Engineering at the University of Wisconsin in Madison. He received his Ph.D. from the University of Minnesota in 1966. He taught chemical engineering at the University of Waterloo in Canada, from 1966 to 1970, and at the State University of New York at Buffalo, from 1970 to 1976. Professor Ray has acted as consultant to the petroleum, chemical, and metals industries, and has contributed numerous articles to the technical literature in the areas of polymerization processes, chemical reaction engineering, process modeling, optimization, and process dynamics and control. He is coauthor of a monograph, "Process Optimization," published in 1973, and author of *Advanced Process Control*, which appeared in 1981. This latter book has also been published in Russian. Professor Ray is also coeditor of two volumes: *Distributed Parameter Systems* (1978) and *Dynamics and Modeling of Reacting Systems* (1980). In 1969, Professor Ray received the D. P. Eckman Award of the American Automatic Control Council and, in 1973-1974, he spent a year as a Guggenheim Fellow in Europe. In 1981, he received the Arthur K. Doolittle Award of the Organic Coatings and Plastics Division of the American Chemical Society and also the Automatica Prize Paper Award of the International Federation of Automatic Control. More recently, he was the recipient of the 1982 Professional Progress Award of the American Institute of Chemical Engineers.

## Out of Control



"and our control engineers apply highly advanced, state-of-the-art techniques for selecting pole-zero locations."